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by

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ABSTRACT

A state-of-the-art review of the processes currently being developed for the removal of nitrogen oxides (NO_x) from power plant stack gas was conducted. Included within the 48 processes discussed in the report are: dry NO_x processes, dry simultaneous NO_x - SO_x processes, wet NO_x processes, and wet simultaneous NO_x - SO_x processes. The major sections in each technical evaluation for each process included detailed process description containing a simplified block flow diagram, the current status of development of the process, the raw material and utility requirements, the published economics, the technical and environmental considerations, and the overall advantages and disadvantages of the process. In addition to this review of the current NO_x flue gas treatment (FGT) technology, eight of these processes were recommended as candidates for preliminary economic analysis in the next phase of the study. The information for this report was gathered during the first half of 1977 and work was completed as of July 1977. The report was prepared by the Tennessee Valley Authority under a project cofunded by the U.S. Environmental Protection Agency and the Electric Power Research Institute.

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ABBREVIATIONS AND CONVERSION FACTORS

ABBREVIATIONS

aft ³	actual cubic feet	kWh	kilowatthour
bbl	barrel	l	liter
Btu	British thermal unit	lb	pound
°C	degrees Centigrade	k	thousand
cm	centimeter	m	meter
dia	diameter	M	million
ESP	electrostatic precipitator	mg	milligram
°F	degrees Fahrenheit	min	minute
FGD	flue gas desulfurization	mm	millimeter
FGT	flue gas treatment	mol	mole
ft	feet	MW	megawatt
ft/sec	feet per second	MW equiv	megawatt equivalent
g	gram	Nm ³	normal cubic meter
G	billion	ppm	parts per million
gal	gallon	SCR	selective catalytic reduction
gpm	gallons per minute	sft ³ /hr	standard cubic feet per hour
gr	grain	sft ³ /min	standard cubic feet per minute
hr	hour	sec	second
in.	inch	sv	space velocity
kg	kilogram	vol	volume
kl	kiloliter	wt	weight
kW	kilowatt	yr	year

CONVERSION FACTORS

To convert from	To	Multiply by
British thermal unit	gram-calories	252
degrees Fahrenheit-32	degrees Centigrade	0.5555
dollars	yen	0.00333
feet	centimeters	30.48
cubic feet	cubic meters	0.02832
feet per minute	centimeters per second	0.508
cubic feet per minute	cubic meters per second	0.000472
gallons	liters	3.785
gallons per minute	liters per second	0.06308
gallons per thousand actual cubic feet (50°C)	liters per normal cubic meter	0.1608
grains (troy)	grams	0.0648
grains per cubic foot	grams per cubic meters	2.288
megawatt (electric)	normal cubic meters per hour	0.000333
megawatt (electric)	standard cubic feet per minute	0.000535
mills per kilowatthour	yen per kiloliter of oil	1248. ^a
pounds	kilograms	0.4536
standard cubic feet per minute (32°F)	normal cubic meters per hour (0°C)	1.695
tons (short)	metric tons	0.90718
tons (long)	metric tons	1.016
tons per hour	kilograms per second	0.252

a. Assuming 300 yen/dollar, 144,000 Btu/gal of oil, and 9,000 Btu/kWh.

Executive Summary

With the increasing application of particulate removal systems and the expansion of the development and application of flue gas desulfurization (FGD) systems, regulatory attention within the U.S. Environmental Protection Agency (EPA) has begun to shift to controlling a third emission component present in combustion flue gases, nitrogen oxides (NO_x). Largely, this shift is due to the inability of automobile manufacturers to develop a viable NO_x emission control technology for mobile sources without incurring significant fuel economy penalties. More recently, the 1977 Clean Air Act Amendments have increased the impetus for more stringent NO_x regulations. Combustion modification techniques currently under research by the Electric Power Research Institute (EPRI) and EPA may provide sufficient control of the power plant contribution to NO_x emissions. However, since the success of these processes is unknown at this time and since the ultimate regulatory posture to be adopted regarding NO_x emissions is as yet undefined, alternative, though potentially less cost-effective, approaches cannot be ruled out.

This report covering the first phase of a multiphase NO_x removal process study, is a state-of-the-art survey of all known flue gas denitrification processes currently undergoing development in the U.S. and Japan. Because low NO_x emission limits have been emphasized in Japan in recent years, flue gas denitrification technology is much more diversified in that country; therefore, most of the processes included in the first phase of this study were developed and are being marketed by Japanese companies. During the preparation of this report, various Japanese and American companies were contacted for pertinent technical and economic information outlining their NO_x removal processes. This information and the data obtained from other sources were combined to describe the major technical and economic aspects of each process. Major sections discussed for each process include a process description, the status of development, the reported economics, utility and raw material requirements, technical and environmental considerations, and the advantages and disadvantages. The 48 flue gas denitrification processes currently listed in the literature are included in Table S-1 and are classified into types and subcategories which will be described later. Since essentially no information is available on 6 of the processes, only 42 processes are described in the report. In addition to describing the

TABLE S-1. CURRENT FLUE GAS DENITRIFICATION PROCESSES

Dry processes	Wet processes
Selective catalytic reduction Asahi Glass^a Eneron Exxon Hitachi, Ltd. Hitachi Zosen JGC Paradox Kobe Steel Kurabo Knorca Kureha Mitsubishi Heavy Industries Mitsubishi Kakoki Kaisha Mitsubishi Petrochemical Mitsui Engineering and Shipbuilding Mitsui Toatsu Nippon Kokan^a Sumitomo Chemical Sumitomo Heavy Industries^b Takeda Ube Unitika^b Universal Oil Products-Shell CuO^b Nonselective catalytic reduction The Ralph M. Parsons Selective noncatalytic reduction Exxon Thermal Denox Adsorption Foster Wheeler-Bergbau Forschung Radiation Ebara-JAERI Uncertain Princeton Chemical Research^a	Absorption-reduction Asahi Chemical Chisso Engineering Kureha Mitsui Engineering and Shipbuilding Pittsburgh Environmental and Energy Systems Oxidation-absorption-reduction Chiyoda Thoroughbred 102 Ishikawajima-Harima Heavy Industries Mitsubishi Heavy Industries Moretana Calcium Moretana Sodium Osaka Soda^a Shirogene^a Absorption-oxidation Hodogaya^a Kobe Steel MON Alkali Permanganate Nissan Engineering Oxidation-absorption Kawasaki Heavy Industries Tokyo Electric-Mitsubishi HI Ube

a. Essentially no information available.

b. These companies have two dry processes: (1) NO_x-only and (2) SO₂-NO_x.

various alternative processes, another major objective of this first phase is to recommend processes for preliminary economic analysis as a second phase study.

COMPARISON OF DRY AND WET NO_x REMOVAL PROCESSES

The flue gas denitrification processes can be initially separated into two types, wet or dry, depending on whether or not the NO_x is absorbed into an aqueous solution. With a few notable exceptions the dry processes are NO_x-only removal systems while in general the wet processes are simultaneous sulfur dioxide (SO₂) and NO_x removal systems. Although there are a few examples of wet NO_x-only technology, these processes were originally developed for treatment of nitric acid (HNO₃) plant tail gas and may not compete economically with the much simpler dry NO_x-only units. Therefore, most of the initial development work on wet NO_x removal processes has been in adapting the existing wet FGD technology to simultaneously remove both SO₂ and NO_x.

For a variety of reasons, including simplicity, more favorable economics, and the fact that most existing power plants in Japan operate with low-sulfur (S) oil as fuel with small amounts of particulate and SO₂ flue gas emissions, the dry NO_x-only removal processes seemed the most promising and were developed first. The initial research for most of the wet processes was begun later and, hence, the dry processes as a group have been more extensively tested and are more commercially acceptable.

Although there are many different types of dry and wet processes, in most cases the dry processes have the following advantages over the wet processes.

1. Lower projected total capital investment and lower annual revenue requirements
2. Simpler process with few equipment requirements
3. Higher NO_x removal efficiency (>90%)
4. More extensive tests in large units (oil- and/or gas-fired boilers)
5. No waste stream generation

However these dry systems also have the following disadvantages.

1. More sensitive to inlet particulate levels
2. Requirement for ammonia (NH₃) from either an energy-sensitive source (natural gas) or more expensive coal gasification methods
3. Possible emission of NH₃ and ammonium sulfates $[(NH_4)_2SO_4]$ and bisulfates (NH₄HSO₄); precipitation of same may create fouling of downstream equipment
4. Relatively higher reaction temperatures (350-400°C) which must be located in the power generation cycle before the air preheater or must be attained by auxiliary heating after the preheater

The most critical of these disadvantages, particularly for the U.S. utility industry with its heavy reliance on coal for power generation, is the sensitivity of these processes to inlet particulate levels. However, major research is now underway to develop methods to enable dry systems to

handle flue gas with high particulate loading. Evaluations are being performed on coal-fired flue gas; however, these tests have not been executed on a very large scale.

Another disadvantage of the dry, selective catalytic reduction (SCR) processes is that the ideal catalyst location may be in the region between the economizer outlet and the air preheater inlet and, hence, the process is intimately involved in the power generation cycle. Therefore, if problems of operating these processes occur, the adverse impacts on the basic utility operations may be greater.

In addition to the above-mentioned disadvantages, the long-term supply of NH_3 for these dry NO_x removal processes is a potential problem. NH_3 is the reducing agent for converting NO_x to molecular nitrogen (N_2) for the SCR processes (which comprises nearly all of the dry processes and about half of all the NO_x removal processes--see Table S-1) and the selective non-catalytic reduction process. With an $\text{NH}_3:\text{NO}_x$ mol ratio of about 1:1 a single 500-MW coal-fired power plant (600 ppm NO_x in the flue gas) would consume about 5950 tons/yr of liquid anhydrous NH_3 . In view of the continuing increase in the world's demand of NH_3 and NH_3 -based fertilizers, the availability of NH_3 for larger numbers of these dry NO_x removal units warrants concern and further investigation.

The wet NO_x removal processes have certain general advantages and disadvantages as compared with the dry systems. These major advantages include:

1. Simultaneous SO_2 - NO_x removal may be a potential economic advantage
2. Relatively insensitive to flue gas particulates
3. Higher SO_2 removal (>95%)

On the other hand the major disadvantages of these wet systems include:

1. More expensive processes due to the insolubility of NO_x in aqueous solutions
2. Formation of nitrates (NO_3^-) and other potential water pollutants
3. More extensive equipment requirements
4. Formation of low-demand byproducts
5. Flue gas reheat required (however, if a wet SO_2 removal system were used in series with a wet removal system for NO_x only, the reheat would have already been incorporated into the design)
6. Only moderate NO_x removal
7. Application of some processes may be limited to flue gas with high $\text{SO}_x:\text{NO}_x$ ratio

The two primary disadvantages of the wet systems are the high capital and operating costs and the formation of NO_3^- -containing wastewater. The generation of NO_3^- salts in most of these processes results in the need to remove these salts from the effluent by either evaporation or biological treatment.

Another important factor which must be considered in the application of certain wet NO_x removal processes is the minimum $\text{SO}_x:\text{NO}_x$ ratios required. It may not be feasible to operate wet NO_x removal processes using flue gas from Western U.S. coals, which characteristically possess low amounts of S, since sufficient $\text{SO}_x:\text{NO}_x$ ratios may not be achieved for adequate NO_x removal.

DRY NO_x REMOVAL PROCESSES

The dry flue gas denitrification processes can be subdivided into five major categories. These categories and the number of processes of each type included in this study are shown below.

Category	Number of processes
Selective catalytic reduction	22
Nonselective catalytic reduction	1
Selective noncatalytic reduction	1
Absorption	1
Radiation	1

Table S-2 shows a general comparison of these various types of dry processes.

As is readily apparent from this list, the overwhelming majority of the dry systems currently undergoing development are based on the SCR method and use NH_3 as the reductant. In this method the anhydrous NH_3 is injected into the flue gas after the boiler economizer and the resulting mixture is passed over a proprietary base-metal catalyst. The NH_3 selectively reduces the NO_x to molecular N_2 which then passes out of the NO_x removal system and into the boiler air heater.

The primary disadvantage associated with the SCR method when applied to coal-fired flue gas is the sensitivity of the catalyst to the higher particulate levels in the flue gas. Although most of these processes have been designed to minimize the effects of dust, either through the type of reactor used or shape of the catalyst particles, this development work was done using heavy oil-fired flue gas. Additional detailed pilot-plant testing on coal-fired flue gas will be needed and is underway by some companies to confirm the ability of these innovations to handle the higher particulate loadings associated with coal combustion. Upon completion of these tests, further development on even larger scale will be necessary.

One additional potential problem is the formation and precipitation of ammonium bisulfate (NH_4HSO_4) downstream from the reduction reactor, particularly in the boiler air heater. The NH_4HSO_4 formation is dependent upon temperature and the NH_3 and sulfur trioxide (SO_3) concentrations. It may become necessary to decrease the mol ratio of $\text{NH}_3:\text{NO}_x$ and thus decrease the denitrification efficiency below 90% to prevent the formation of NH_4HSO_4 . The use of a catalyst for the decomposition of NH_3 would provide an alternative method of control though it would increase complexity of capital investment. The development of such catalysts is being conducted by some companies.

TABLE S-2. COMPARISON OF DRY NO_x REMOVAL PROCESSES

Process characteristics ^a	Dry NO _x removal process type				
	Selective catalytic reduction	Nonselective catalytic reduction	Selective noncatalytic reduction	Adsorption	Radiation
Simultaneous SO ₂ -NO _x removal	- _b	X	-	X	X
Achieves moderate SO ₂ removal (>85%)	-	X	-	X	X
Achieves high NO _x removal (>90%)	X	X	-	-	X
Operating conditions	-	-	-	X	X
Produces waste stream	-	-	-	-	-
Uses NH ₃	X	-	X	-	-
Forms NH ₄ HSO ₄	X	-	X	-	-
Operates with sensitivity to particulates	X	-	X	X	-
Produces marketable byproduct	- _b	X	-	X	-
Current development status	-	-	-	-	-
Tested on coal-fired flue gas	-	-	-	X	-
Tested on pilot plant or larger scale	X	-	X	X	X

a. An "X" indicates the process has this characteristic.
b. Depends on process.

The nonselective catalytic reduction processes involve the injection of a fuel or reducing gas into the radiant zone of the boiler to chemically bind the excess oxygen (O_2) and thus minimize the formation of oxides of S and N. For economical operation, this use of a reducing gas will be combined with combustion modifications such as firing with a slightly substoichiometric amount of air to decrease the consumption of reducing gas as much as possible. As this O_2 -deficient flue gas containing some SO_2 and NO_x is passed over a nonnoble metal catalyst, the SO_2 and NO_x are reduced to hydrogen sulfide (H_2S) and molecular N_2 . The H_2S is then removed in a conventional Stretford unit and the remaining flue gas is exhausted through the stack. This type of process, in addition to simultaneously removing SO_2 and NO_x , produces elemental S as a marketable byproduct. The major disadvantages include the expense of the reducing gas and the possibility of increased corrosion in the boiler due to the high temperature reducing atmosphere.

In the selective noncatalytic reduction processes the NH_3 is injected directly into the upper portion of the boiler to selectively reduce the NO_x to molecular N_2 . This procedure eliminates the need for any supplemental equipment downstream and results in a process scheme with minimum capital investment. Unfortunately it has the major disadvantages of requiring a higher $NH_3:NO_x$ mol ratio and thereby potentially creating more problems with NH_4HSO_4 than catalytic processes, operating in a very narrow temperature range, and yielding only low NO_x removal (40-60%). There is also uncertainty concerning the effects of flyash from coal-fired flue gas upon the NO_x removal efficiency of this process.

The dry adsorption processes are based on the use of activated carbon (C) to adsorb both SO_2 and NO_x from the flue gas. The adsorbent is regenerated at a high temperature to yield a concentrated off-gas stream of SO_2 and molecular N_2 . This SO_2 could be used to generate elemental S or byproduct sulfuric acid (H_2SO_4).

The disadvantages of this type process include low NO_x removal efficiency and high C loss.

The radiation process is unique in that the flue gas is bombarded with an electron beam. This radiation converts the particulates, SO_2 , and NO_x into a powdery, complex mixture which is then removed in an electrostatic precipitator (ESP). The major disadvantages include high initial capital investment, high annual revenue requirements, secondary waste disposal problem, and low (80%) SO_2 removal efficiency.

WET NO_x REMOVAL PROCESSES

The wet denitrification processes can also be subdivided into four major categories. These categories and the number of processes of each type included in this study is as follows:

Category	Number of processes
Absorption-reduction	5
Oxidation-absorption-reduction	5
Absorption-oxidation	3
Oxidation-absorption	3

An overall comparison of these categories of wet processes is given in Table S-3.

The absorption-reduction technology is based on using a water (H_2O)-soluble ferrous-chelating compound; e.g., Asahi Chemical Industry Company uses ferrous ethylene diamine tetraacetic acid (Fe^{+2} -EDTA) as a catalyst to aid in the absorption of the relatively insoluble NO_x . These ferrous compounds have the ability to form complexes with the NO_x and thus promote the absorption of the NO_x (primarily NO). Once in the solution the NO_x can be reduced by the absorbed SO_2 [i.e., the sulfite ($SO_3^{=}$) ion] to form molecular N_2 or reduced N compounds.

Even with the use of this absorption catalyst, the NO is sufficiently insoluble that the gas-liquid contact time must be increased; therefore, high liquid-to-gas (L/G) ratios and low superficial gas velocities are required. The L/G ratio in the absorber is normally about 15 l/Nm^3 (93 gal/kaft³ at 127°F) and the superficial gas velocity is in the range of 1-3 m/sec (3-10 ft/sec).

Unfortunately these absorption-reduction processes also have other significant disadvantages in addition to the large absorption section. Most of these processes have extensive equipment requirements and the NO_x removal efficiencies are also sensitive to the inlet flue gas composition, particularly the inlet O_2 and SO_2 concentrations. These processes have only been tested in bench-scale units for treating oil-fired flue gas.

The oxidation-absorption-reduction processes, on the other hand, are in most cases simple modifications of commercially available FGD technology. To use the conventional FGD scrubbers, the insoluble NO in the flue gas must be chemically converted to increase its solubility. A gas-phase oxidant, such as ozone (O_3) or chlorine dioxide (ClO_2), is injected into the flue gas to selectively oxidize insoluble NO to the more soluble NO_2 . For processes using H_2O -soluble absorbents and thus generating H_2O -soluble sulfites when absorbing the SO_2 from the flue gas, the simple injection of a gas-phase oxidant is all that is necessary to convert a conventional FGD system into a simultaneous SO_2 - NO_x removal system. If, however, the SO_2 absorbent is relatively insoluble in aqueous solution and forms insoluble $SO_3^{=}$, for example limestone scrubbing, the simple addition of a gas-phase oxidant will not yield good NO_x removal. An H_2O -soluble catalyst must also be present in the solution to supplement the gas-phase oxidant and give good NO_x removal efficiency.

Oxidation-absorption-reduction processes, then, are commercially available FGD systems which have been modified to give both SO_2 and NO_x

TABLE S-3. COMPARISON OF WET NO_x REMOVAL PROCESSES

Process characteristics ^a	Wet NO _x removal process type			
	Absorption-oxidation	Oxidation-absorption	Absorption-oxidation	Absorption-reduction
Simultaneous SO ₂ -NO _x removal	-	X ^b	X	X
Achieves high SO ₂ removal (>95%)	-	X	X	X
Achieves moderate NO _x removal (>85%)	X	X	X	-
Operating conditions				
Requires absorption catalyst	-	-	X ^b	X
Requires liquid-phase oxidant	X	-	-	-
Requires gas-phase oxidant	-	X	X	-
Requires large absorber	X	X	-	X
Requires flue gas reheat	X	X	X	X
Forms nitrate salts in wastewater	X	X	X ^b	-
Requires specific range of flue gas constituents	X	-	X ^b	X
Current development status				
Tested on coal-fired flue gas	-	X ^b	-	X ^b
Tested on pilot plant or larger scale	-	X	X	X ^b

a. An "X" indicates the process has this characteristic.

b. Depends on process.

removal. Other advantages include good NO_x removal efficiencies (85-90%), excellent SO_2 removal efficiencies (>95%), and these processes are also relatively insensitive to the inlet flue gas composition.

However, these types of processes have two serious drawbacks. The most serious is probably the cost of the gas-phase oxidant. For the rapid, selective oxidation of NO, either O_3 or ClO_2 must be used. Both are extremely expensive and must be generated onsite (5, 19). O_3 is the more expensive of the two but has the advantage of not releasing any additional pollutants into the flue gas. ClO_2 , although costing only about one-fourth as much as O_3 , unfortunately releases additional Cl^- and NO_3^- into the scrubbing solution. The second major problem with the oxidation-absorption-reduction processes, regardless of which gas-phase oxidant is used, is that they generated a wastewater NO_3^- stream which must be treated before it can be released. Depending on the process involved, the percentage of the absorbed NO_x converted to NO_3^- salts ranges from 10-50%. The two most common wastewater treatment methods for this soluble NO_3^- are evaporation and biological denitrification.

Although the oxidation-absorption-reduction and absorption-reduction processes have several major disadvantages, the absorption-oxidation and oxidation-absorption processes have these same problems as well as several additional drawbacks. The absorption-oxidation processes have similar problems to those given for the absorption-reduction processes, i.e., forcing the insoluble NO into the aqueous scrubbing solution and hence requiring a large and expensive absorber. Also, these processes are further complicated by the fact that they use a liquid-phase oxidant, either a permanganate or hypochlorite solution, to convert the absorbed NO_x to NO_3^- salts. This conversion of the absorbed NO_x to highly soluble NO_3^- salts is undesirable since these NO_3^- salts are difficult to remove and cannot be released as a wastewater stream. The use of an expensive liquid-phase oxidant prevents the introduction of the ferrous-chelating compound to aid in the absorption of NO_x . For economic reasons the use of a liquid-phase oxidant also limits these processes to NO_x removal only since the oxidant would readily convert the SO_3^{2-} ion, formed from the absorption of SO_2 , to sulfate (SO_4^{2-}). Thus the SO_2 must be removed before entering the NO_x absorber to prevent the excessive consumption of expensive oxidant.

The oxidation-absorption processes, unlike the other classes of wet flue gas denitrification processes, have no common treatment mechanism. These denitrification systems are similar only in the fact that they contain an initial gas-phase oxidation stage and follow this with an absorption stage. The example processes range from the straightforward gas-phase oxidation and absorption to the equimolar absorption of NO and NO_2 using a recycle NO_2 -rich stream.

In addition to their general class disadvantages, such as the formation of wastewater NO_3^- solutions and the requirement for a gas-phase oxidant, each type of oxidation-absorption has a unique set of treatment problems. The straightforward oxidation-absorption type uses a high oxidant: NO_x mol ratio and an SO_2 -free flue gas source to recover the NO_x as a weak HNO_3

solution. The excess oxidant must then be removed in a separate closed-loop absorption section. The other type of oxidation-absorption process, equimolar absorption of NO and NO₂, requires the generation of an NO₂-rich recycle stream and a two-stage NO_x absorber. The latter is needed since this equimolar absorption mechanism is limited to a final outlet NO_x concentration of 150-200 ppm. Further NO_x removal (i.e., 90% overall removal) requires the use of a gas-phase oxidant and a second absorption stage.

COMPARISON OF THE ADVANTAGES AND DISADVANTAGES OF THE INDIVIDUAL FLUE GAS DENITRIFICATION PROCESSES

A detailed technical evaluation of each of the flue gas denitrification processes included in this study was prepared from information already available in the public domain and from direct contacts with the various process developers. After this information had been assimilated into several sections including a process description, a block flow diagram, technical and environmental considerations, and the current status of development, a list of advantages and disadvantages for each of the individual flue gas denitrification processes was prepared. Table S-4 contains a comparison of the various advantages while Table S-5 shows the disadvantages of each of the flue gas denitrification processes included in this study. These advantages and disadvantages are based on information available at the present time and can be expected to change as new information becomes available. Also, the stated technology may not be optimum for example, the use of auxiliary heaters by most of the dry processes may be circumvented in future designs.

CONCLUSIONS AND RECOMMENDATIONS

The most tested and advanced NO_x flue gas treatment (FGT) method now is SCR. Several commercial, oil-fired SCR denitrification units have been operated and about half of the total denitrification processes included in this report are the SCR type. However, most of the overall FGT development work performed to date has been with bench-scale and pilot-plant size operations on gas- or oil-fired flue gas. Also, there are several drawbacks to be considered and solved in future development regarding both dry and wet NO_x removal processes. Therefore, before any FGT processes are feasible for application to commercial, coal-fired power plants, further testing must be done on pilot-plant and prototype units with coal-fired flue gas. It should be noted, too, that the economics for the processes reported herein may be subject to revision as the processes are developed further on a larger scale.

A prime objective of this study, in addition to being a state-of-the-art review of all NO_x processes undergoing development, is to recommend processes for further evaluation in the second phase (Phase II) of this NO_x removal process study. This second phase will be a preliminary economic analysis of the processes selected during this first phase.

TABLE S-4. COMPARISON OF THE ADVANTAGES OF THE
CURRENT FLUE GAS DENITRIFICATION PROCESSES^a

Advantage ^c	Hot NO _x Removal Processes ^d										Dry NO _x Removal Processes ^d									
Removes NO _x & SO ₂ simultaneously.																				
Achieves (> 90%) NO _x removal.																				
Achieves (> 95%) SO ₂ removal.																				
Produces potentially marketable byproduct.																				
a. Elemental sulfur																				
b. Sulfuric acid																				
c. Oxygen																				
d. Other																				
Has been tested on coal-fired flue gas on pilot-plant scale																				
Has been applied to flue gas from a commercial oil-fired boiler.																				
Is a slight modification of a commercially available FGD system.																				
Operates with full particulate loading.																				
Operates with moderate particulate loading.																				
Claims less than 10 ppm by volume H ₂ S in treated flue gas.																				
Claims full turndown capability.																				
Operates between 100 & 200°C, which may require only negligible reheat.																				
Does not require chemical raw materials.																				
Requires no additional post-boiler processing equipment.																				
Uses catalyst which, when spent, has other potential applications.																				

a. Based on the latest information, other advantages and disadvantages may become apparent as more data are released.

b. AI: Absorption reduction R: Radiation

OA: Oxidation-absorption-reduction SCR: Selective catalytic reduction

OC: Oxidation-absorption SMR: Selective noncatalytic reduction

AO: Absorption-oxidation A: Adsorption

NCR: Nonselective catalytic reduction

c. An "X" denotes the process has this characteristic.

d. Sodium sulfate.

e. Ammonium sulfate.

f. Concentrated SO₂ (g)

g. 60% HNO₃.

h. Coke oven plant.

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disadvantages may become apparent as more data are released.

After a detailed technical review of the currently available flue gas denitrification processes had been completed, eight processes were recommended for further study based on the following criteria:

- Technical considerations
- Development status
- Representative sample

The reasons for basing the selection on the technical feasibility of the processes are obvious in that to be considered the process must be able to remove NO_x from flue gas and also be potentially applicable to coal-fired boilers. Other technical considerations involved in the selection process included NO_x removal efficiency, generation of waste streams, background of process developers, and system complexity. Also, to rate the process highly, some type of modification must have been added which would minimize the effects of the increased particulates, NO_x , and Cl^- associated with coal combustion.

The second major selection criterion was the development status of the process. The ideal status of development would be a process which had been extensively tested in a commercial-scale unit (>50 MW) treating flue gas from a coal-fired boiler. Since only one or two of the processes have been extensively tested on coal-fired flue gas, the developmental status criterion was reduced to simply the size of the test unit. For this study, the following classification system for the test units (and for comparison purposes, the number of examples at each stage at the present time) was specified.

	Size	Number of processes
Commercial	MW ≥ 50	5
Prototype	$5 \leq \text{MW} < 50$	10
Pilot plant	$0.5 \leq \text{MW} < 5$	14
Bench scale	MW ≤ 0.5	8
Conceptual	-	4

Except for the Exxon Thermal process, which is a selective noncatalytic reduction process, all of the commercial units currently operating are based on the dry SCR technology. The dry SCR also represents four of the prototype units with four others being various types of wet processes. The pilot-plant units are primarily dry SCR processes with a few wet oxidation-absorption-reduction and a few wet absorption-reduction processes, whereas the bench-scale units include most of the wet absorption-reduction and a variety of dry processes.

Since very few of the processes have been tested on coal-fired flue gas and only one class of processes has reached the commercial stage of development, the third and possibly the most important selection criterion, a representative sample, was added. If only the previously mentioned criteria were used, the preliminary economic analysis in Phase II would include only two broad classes of NO_x removal processes, dry SCR and wet oxidation-absorption-reduction. Thus, to provide a good comparison of the various

available and potentially available technologies, a third selection criterion, the desire to obtain a representative sample of the alternative processes, was included. For this reason the Asahi Chemical process, the Ishikawajima-Harima Heavy Industries process, and the MON Alkali Permanganate process were chosen to represent the absorption-reduction, oxidation-absorption-reduction, and the absorption-oxidation processes respectively. The other five processes were selected based on both technical considerations and development status. The eight processes chosen for preliminary economic analysis are listed in Table S-6.

TABLE S-6. PROCESSES RECOMMENDED FOR FURTHER STUDY IN PHASE II

Process	Type of process (classification)
UOP Shell Copper Oxide	Dry Simultaneous SO ₂ -NO _x (Selective catalytic reduction)
UOP Shell Copper Oxide	Dry NO _x only (Selective catalytic reduction)
Hitachi Zosen	Dry NO _x only (Selective catalytic reduction)
Kurabo Knorca	Dry NO _x only (Selective catalytic reduction)
Moretana Calcium	Wet simultaneous SO ₂ -NO _x (Oxidation-absorption-reduction)
Ishikawajima-Harima Heavy Industries	Wet simultaneous SO ₂ -NO _x (Oxidation-absorption-reduction)
Asahi Chemical	Wet simultaneous SO ₂ -NO _x (Absorption-reduction)
MON Alkali Permanganate	Wet NO _x only (Absorption-oxidation)

At first glance the recommendation of four dry SCR processes for further study would seem to contradict the desire for a representative sample; however 22 of the 42 processes included in this study are based on the dry SCR technology. In addition, each of these four processes involve variations in this SCR technology. For example, the UOP process can be operated for either simultaneous SO₂-NO_x removal or NO_x-only removal and uses a unique parallel passage reactor to minimize particulate problems. The Hitachi Shipbuilding and Engineering process (Hitachi Zosen), on the other hand, uses a honeycomb-shaped catalyst, whereas the Kurabo Knorca

system utilizes a moving-bed reactor to minimize the effects of dust. Since plugging by dust is expected to be a major problem with the dry SCR processes, analyzing these three systems will allow a comparison of the various approaches.

The recommendation of two wet oxidation-absorption-reduction processes would also appear to be contrary to the desire for a representative sample. Upon closer examination, however, the Ishikawajima-Harima Heavy Industries process is based on using O_3 as the gas-phase oxidant while the Fuji Kasui-Sumitomo Metals' Moretana Calcium process uses ClO_2 . These two oxidants, although serving the same purpose, involve different economics and different technical problems in their use.

The selection of these processes should, at the end of Phase II, allow comparison of various types of wet simultaneous SO_2 - NO_x processes, dry versus wet simultaneous SO_2 - NO_x processes, dry versus wet NO_x -only processes, and simultaneous SO_2 - NO_x processes versus NO_x -only processes combined with an FGD system.

In some cases there are several other processes similar to those chosen for further study in the second phase. Their elimination should not imply that these processes are inferior, but rather that these processes represent similar technologies and as such do not possess significant differences from the processes selected.

INTRODUCTION

Man-made nitrogen oxides (NO_x) are classified as two types, depending upon their source--stationary or mobile. Each source is responsible for approximately half of the total NO_x emissions. These stationary and mobile sources can be further divided into the various groups listed in Table 1. The estimated total amounts and the percentages of the total amount of man-made NO_x released from each source for the years 1970, 1972, and 1974 are also shown. During this period the only two groups with increasing NO_x emissions were the mobile sources, particularly automobiles and trucks, and the fuel combustion (boiler) group of stationary sources.

The NO_x emission limits for the mobile sources were formulated in 1971 by the U.S. Environmental Protection Agency (EPA) and originally required compliance by the 1976 model year. However, due to technical, economic, and other considerations, these standards for automobiles have been delayed once and are expected to be postponed again. Thus the brunt of decreasing the man-made NO_x emissions, at least for the near future, will be directed toward the stationary sources. Since the fuel combustion group represents 90-95% of all the emissions from stationary sources, this group appears the most likely to undergo more stringent regulation.

The fuel combustion group can be split into other subgroups according to the type of fuel used and the type of operation being performed. As one would expect, the six fuel combustion sources emitting the largest quantities of NO_x are utility and industrial boilers burning coal, oil, or gas. These six sources and the estimated amounts of NO_x emitted for each are listed in Table 2. The largest source of NO_x in the fuel combustion group is coal-fired utility boilers followed by oil-fired industrial boilers and utility boilers; approximately 30% of all stationary source NO_x is emitted by coal-fired utility boilers.

Although NO_x is present in relatively minor amounts in the flue gas (<0.1% by volume of the total flue gas), a single 500-MW coal-fired power plant releases approximately 10,800 tons/yr of NO_x to the atmosphere (assuming 600 ppm of NO_x in the flue gas). This NO_x in the flue gas is generated during combustion from either the nitrogen-containing (N) compounds in the fuel (fuel NO_x) or the reaction of molecular nitrogen (N_2) and oxygen (O_2) at high temperatures (thermal NO_x). The portion of the total NO_x emissions from each of these sources is a function of many variables and is relatively site-specific.

TABLE 1. NO_x EMISSIONS IN THE UNITED STATES (39)

Source	Annual NO _x emissions					
	1970		1972		1974	
	Amount, Mtons ^a	% of total NO _x	Amount, Mtons ^a	% of total NO _x	Amount, Mtons ^a	% of total NO _x
Mobile						
Highway	6.9	33.8	7.9	35.6	8.1	36.0
Nonhighway	2.4	11.8	2.6	11.7	2.6	11.6
Subtotal	9.3	45.6	10.5	47.3	10.7	47.6
Stationary						
Fuel combustion	10.1	49.5	10.8	48.6	11.0	48.9
Industrial processes (noncombustion)	0.6	2.9	0.6	2.7	0.6	2.7
Solid waste	0.3	1.5	0.2	0.9	0.1	0.4
Miscellaneous	0.1	0.5	0.1	0.5	0.1	0.4
Subtotal	11.1	54.4	11.7	52.7	11.8	52.4
Total NO _x emissions	20.4	100.0	22.2	100.0	22.5	100.0

a. M = one million; tons are metric tons.

With the passage of the Clean Air Act of 1970, EPA formulated and released New Source Performance Standards (NSPS) for NO_x emissions in December 1971. The standards for large boilers [i.e., >250 MBtu/hr (M = one million) (28 MW equiv)]], are shown in Table 3. These standards recognize both the differing amounts of bound N in the fuels (i.e., ranging from 0.2 lb NO_x/MBtu for natural gas with no fuel N to 0.7 lb NO_x/MBtu for coal which contains about 1% fuel N), the size of the utility boiler, and also the best available technology for NO_x control.

TABLE 2. NO_x EMISSIONS FROM SELECTED STATIONARY SOURCES
IN THE U.S. IN 1972 (95)

Stationary source	NO _x emissions	
	Annual amount, metric ton	% of stationary sources
Utility boilers		
Coal fired	3,495,000	30.7
Oil fired	1,114,000	9.8
Gas fired	835,000	7.3
Industrial boilers		
Coal fired	735,000	6.5
Oil fired	1,245,000	10.9
Gas fired	491,000	4.3

TABLE 3. NO_x EMISSION STANDARDS AND PROJECTED RESEARCH OBJECTIVES
FOR LARGE FOSSIL FUEL-FIRED BOILERS

	Present EPA standard (40)		Projected research objectives (95)	
	Lb NO _x /MBtu input to boiler ^a	NO _x , ppm ^b	1980 NO _x , ppm ^b	1985 NO _x , ppm ^b
Gaseous fuel	0.2	150	100	50
Liquid fuel	0.3	225	150	90
Solid fuel	0.7	550	200	100

a. Expressed as NO₂.

b. Calculated at 3% excess O₂, dry basis.

The NSPS may become more stringent since the amount of NO_x released to the atmosphere by utility boilers is increasing. Also, the further development of NO_x control technology increases the probability of stricter NO_x emission regulations in the near future (see projected research objectives in Table 3). This NO_x technology includes both combustion modification, which is receiving major attention in the U.S., and flue gas treatment (FGT), which is being developed primarily in Japan.

Even at the present time, the amount of NO_x released in certain areas of the U.S. is causing the ambient standard to be exceeded. Boiler modifications will probably receive the initial emphasis since these are considered the least expensive methods of controlling NO_x emissions. These techniques, however, are limited to less than 50% reduction in NO_x , primarily because boiler modifications make their major impact by reducing the formation of thermal NO_x .

The percentage reductions in NO_x possible with various types of boiler modifications for the three types of fossil fuels are listed in Table 4. These boiler modifications have their greatest impact on oil- and gas-fired boilers, where most of the NO_x is generated by the thermal mechanism, and less of an impact on coal-fired boilers, where most of the NO_x is formed by the fuel-N mechanism. Unfortunately, the modifications may also result in unstable flame conditions, lower thermal efficiency for the boiler, and increased corrosion inside the boiler. For reductions greater than 50% of the NO_x emissions, which may become necessary in the future, FGT will be required.

Since the costs of FGT processes are considered higher than for boiler modification methods for NO_x reduction, superficially one could deduce that a combination of these means would result in the least expensive system for achieving NO_x reductions of 70-90%. However, if 90% NO_x removal is required, a single FGT system may be less expensive to achieve the full NO_x removal as compared with boiler modification techniques to achieve the first 50% of NO_x removal plus an FGT system for the remaining portion of NO_x removal.

Although boiler modification techniques are now receiving primary attention in the U.S., the FGT processes will certainly become increasingly important. Therefore, the study has been undertaken to assess the development of FGT technology currently being considered both in the U.S. and abroad.

The results of the first-phase activities of this NO_x removal process study are included in this report. The initial phase has a twofold purpose (1) a state-of-the-art technical review of flue gas denitrification processes currently undergoing development work and (2) a screening process in which selected FGT processes are proposed for preliminary economic evaluation in Phase II of the study. The second phase will also recommend some of these processes for further study in Phase III, which will be a detailed economic analysis of the most promising FGT processes for future commercial application.

TABLE 4. EFFECTS OF BOILER MODIFICATIONS TO REDUCE NO_x EMISSIONS
BY FOSSIL FUEL TYPE (95)

Boiler modification	NO _x reduction, %		
	Gas	Oil	Coal
Prevention of thermal NO _x			
Flue gas recirculation	60	20	- ^a
Reduced air preheat	50	40	- ^b
Steam or water injection	60	40	- ^b
Prevention of both thermal and fuel NO _x			
Staged combustion	55	40	40
Low excess air	20	20	20
Reduced heat release rate	20	20	20
Combination of stage combustion, low excess air, and reduced heat release rate	50	35	40
Prevention of fuel NO _x			
Change to fuel with lower % N	- ^c	40	20

a. Not effective.

b. Not competitive.

c. Not applicable.

The main body of this Phase I report is composed of three sections: a short introduction into how NO_x is formed during the combustion of fossil fuels; a discussion of wet NO_x removal; and finally an analysis of dry NO_x removal. A general overview of the various types of flue gas denitrification systems, including a listing of all the FGT processes currently available under the appropriate type of FGT, and a detailed technical discussion of each of the flue gas denitrification processes is included in each of the wet and dry NO_x removal sections. The major parameters which are discussed in the detailed technical evaluation of each process are shown in Table 5.

TABLE 5. OUTLINE OF THE DETAILED TECHNICAL EVALUATION OF EACH PROCESS

Process description and principles of operation

Flow diagram
Evaluation of basic chemistry
Operating conditions and ranges

Status of development

Size of experimental facilities
Duration of testing with acceptable performances
Source of treated gas
Projected commercial availability

Background of process developer

Capability
Accessibility of process to U.S. market

Published economic data

Raw materials, energy, and operation requirements

Raw material consumption
Energy consumption including reheat (steam, fuel, electricity)
Operating manpower
Maintenance
Technical support during routine operation
Latest reported operating conditions and estimated requirements for typical 500-MW unit

Technical considerations

System complexity and process control capability
Sensitivity to inlet gas composition
Alternative treated gas sources
Comparative size of required equipment
Retrofit applicability
Turndown capability
Materials of construction

Environmental considerations

Sensitivity of removal efficiency to control stoichiometry and operating conditions
Potential for removal of other pollutants
Potential problems with waste disposal
Interference of gas species and contaminants of process performance
Work hazards

Critical data gaps and poorly understood phenomena

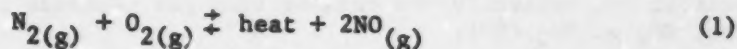
Advantages and disadvantages

GENERAL CHEMISTRY OF NO_x

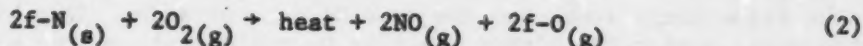
N₂ and O₂ can combine chemically to form one or more of seven oxides of N: nitric oxide (NO), nitrogen dioxide (NO₂), nitrogen trioxide (NO₃), nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃), dinitrogen tetroxide (N₂O₄), and dinitrogen pentoxide (N₂O₅). For most combustion processes, particularly fossil fuel combustion units, the only oxides of N (NO_x) present in significant concentrations in the flue gases are NO and NO₂ with NO representing 90-95% of the total NO_x from the combustion unit (38). The colorless NO in the presence of air will, given sufficient time, oxidize to NO₂. NO₂ is a reddish-brown, toxic gas which in the presence of certain hydrocarbons and sunlight is a precursor for photochemical smog.

During the combustion of fossil fuels, NO_x is formed by two mechanisms: the thermal fixation of atmospheric N₂ and the conversion of fuel-bound N. In both cases the end result is primarily the formation of NO because the residence time in most combustion units is too short for a significant amount of oxidation of NO to NO₂ to occur (25, 99). The reaction mechanisms are complex and are described in more detail in other sources (24, 188). Simplified forms of the overall reactions are shown below.

Thermal fixation:



Fuel-bound N:



The combination of molecular N₂ and O₂ by thermal fixation is an equilibrium reaction with the final concentration of NO primarily dependent on the reaction temperature, but it also varies with the amount of free O₂ and molecular N₂ available in the boiler. The conversion of fuel-bound N, on the other hand, is relatively independent of combustion temperature and forms rapidly even at moderate temperatures. The conversion is primarily dependent on the availability of free O₂ above the combustion zone. During the combustion of fossil fuels containing chemically bound N (oil and coal), portions of the resulting NO_x will be formed by both mechanisms. The exact amounts arising from fuel-bound N and from the thermal fixation of N₂ cannot be calculated from theoretical considerations but vary with specific boiler operating conditions.

In the flow of the flue gas through the boiler, the NO_x is hypothesized to be formed in the following manner. The NO_x formed from fuel-bound N is generated slightly above the actual combustion zone as the gases are beginning to cool and free O_2 is more readily available. At this stage the fuel N is converted to NO with essentially no NO_2 formed. As the flue gases pass through the boiler the rate of conversion of fuel N rapidly declines to essentially negligible levels. The amount of thermal NO_x formed, on the other hand, increases as the gases exit the combustion zone where both the temperature and the O_2 levels are still high. After leaving this zone where NO reaches its maximum value, the flue gases begin to cool very slowly and NO undergoes decomposition by the following equilibrium reaction.



Unfortunately this equilibrium reaction has a high activation energy and once the flue gases reach the section of the boiler where they begin to undergo rapid cooling, the rate of this reaction drops to negligible levels. No further decomposition of NO occurs and the equilibrium NO concentration occurs. The equilibrium NO levels are "frozen" at the temperature where this rapid cooling began.

However, as the NO passes through the cooler portions of the boiler, the NO is gradually, but continuously, converted to NO_2 by the following reaction.



Although thermodynamically favored, the rate of formation of NO_2 in the boiler is very slow and the time available is too short for this reaction to reach equilibrium. The actual amount of NO_2 formed in any boiler is site-specific but typically the exiting flue gas contains less than 10% of the total NO_x as NO_2 (99).

From the previous discussion of the mechanism of NO_x formation then, the total amount of NO_x formed in the specific boiler is primarily a function of the flame temperature and the free O_2 concentration. The higher the flame temperature and/or the higher the free O_2 concentration, the higher the resulting equilibrium concentration of NO in the flue gas. Thus any boiler or operating modifications which minimize either of these operating parameters will decrease the total NO_x emitted from the boiler. Operating conditions which increase flame temperature and/or O_2 concentration in the flue gas, and thereby increase the concentration of NO_x in the flue gas, are as follows:

- Preheating fuel or air (increases temperature)
- Increasing excess air (increases O_2 content)
- Increasing heat rate (increases temperature)
- Increasing load (increases temperature)

Since preheating the fuel or the air, increasing the heat rate, or increasing the boiler load all have the effect of increasing the flame temperature in the boiler, each will contribute to increasing the equilibrium concentration of NO_x . Figures 1 and 2 graphically illustrate the effects of

preheating the air and increasing the load. Modifying these operating variables to decrease the NO_x emissions from the boiler are not desirable alternatives since not preheating the fuel or air will decrease the thermal efficiency of the boiler and decreasing either the heat rate or the boiler load wastes a portion of the boiler capacity.

Various methods have been developed to reduce the free O_2 in the boiler. Decreasing the amount of excess air to the boiler can have a large impact on NO_x emissions, particularly for coal-fired boilers, as can be seen in Figure 3. Redesigning the boilers to prevent the excess air from reaching the hotter areas of the boiler have also received considerable attention as methods to reduce the formation of NO_x . Boiler modifications of this type currently undergoing development include staged combustion, flue gas recirculation, and rearrangement of the burners. The arrangement of the burners and the type of firing can have a significant impact, as shown in Table 6, on the concentration of NO_x in the flue gas.

TABLE 6. CONCENTRATION RANGES OF NO_x FROM COAL-FIRED POWER PLANTS (38)

Type of firing	Typical NO_x concentration, ppm
Vertical	225-310
Horizontally opposed	340-375
Spreader (stoker)	400-470
Tangential (corner)	420-500
Front wall	390-600
Cyclone	800-1200

One other method of reducing NO_x emissions would be to switch to a boiler fuel containing less fuel-bound N. As would be expected, natural gas firing results in the lowest NO_x concentrations since the only NO_x formed is thermal NO_x . Oil-fired boilers generate slightly higher exit NO_x levels since oil contains some fuel-bound N. Coal-fired boilers produce the highest NO_x levels due to the relatively high N content of most coals. Although only a small portion (<30%) of the N in the coal is converted to NO_x , the proportion of the total NO_x emitted which comes from fuel-bound N can be as much as 80% in some coal-fired boilers (24).

As the concentration of bound N in the fuel increases, the actual conversion of this N to NO_x decreases but the total NO_x emitted from the boiler increases. Figure 4 (5) shows this relationship between the NO_x concentration in the flue gas and the percent N in the fuel (for oil-fired boilers). Similar relationships would probably exist for the conversion of fuel N in coal. That is, the conversion of fuel N to NO_x would decrease with increasing fuel N concentration in the coal. The conversion of fuel N is also dependent on the free- O_2 concentration, as shown in Figure 5 (47). Increasing the O_2 concentration in the boiler increases the conversion of fuel-bound N.

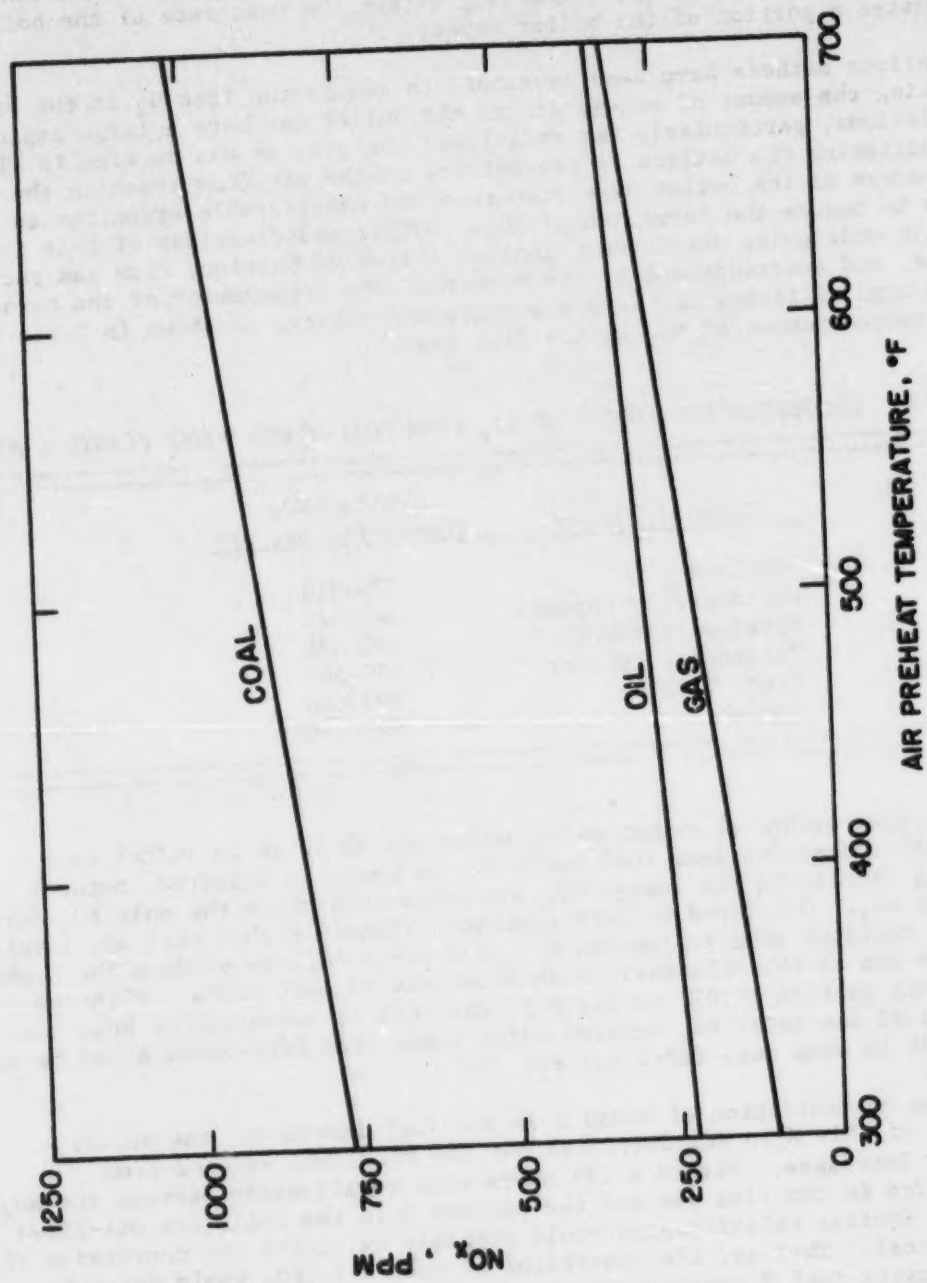


Figure 1. Effect of Air Preheat Temperature on NO_x Emissions (18).

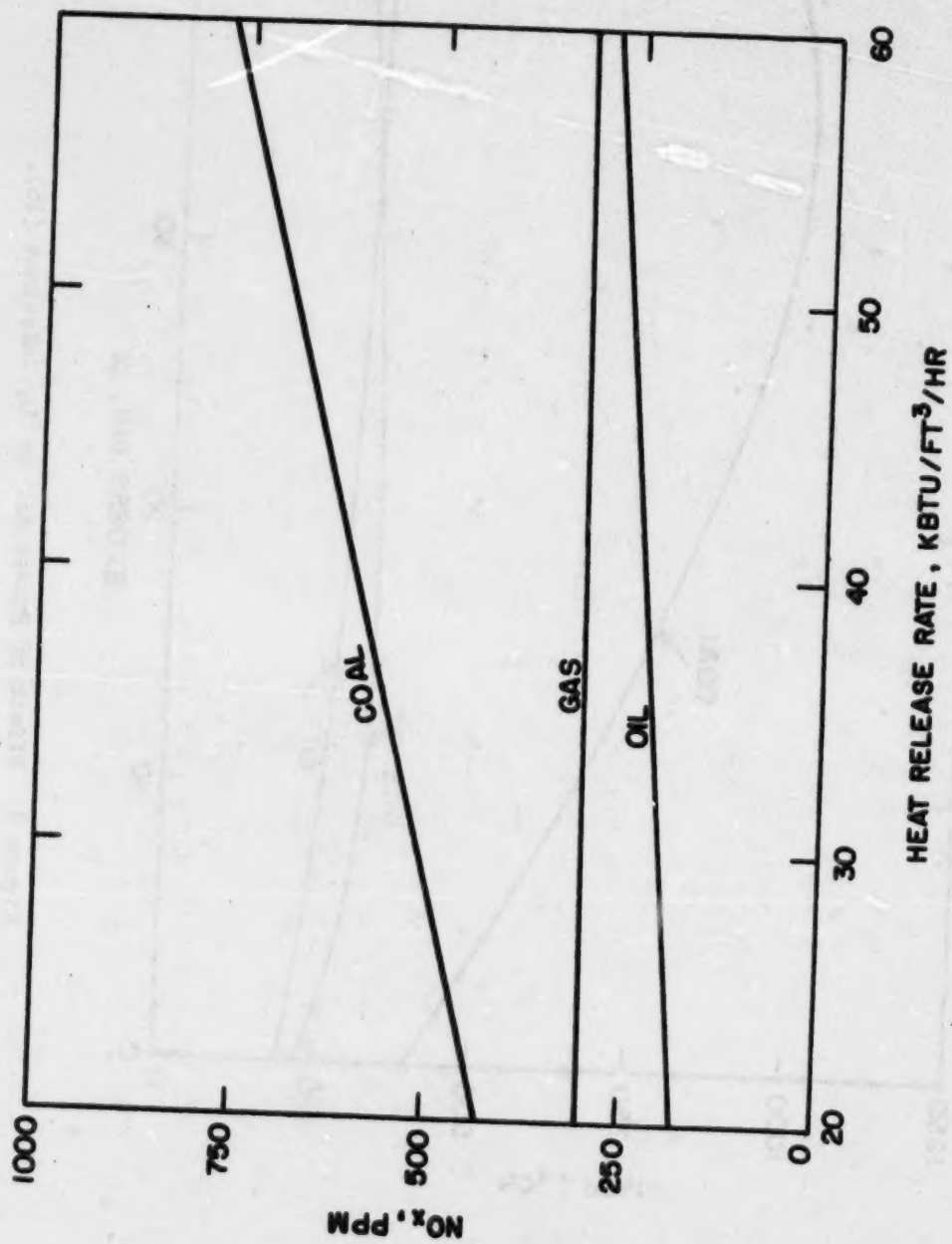


Figure 2. Effect of Heat Release Rate on NO_x Emissions (18).

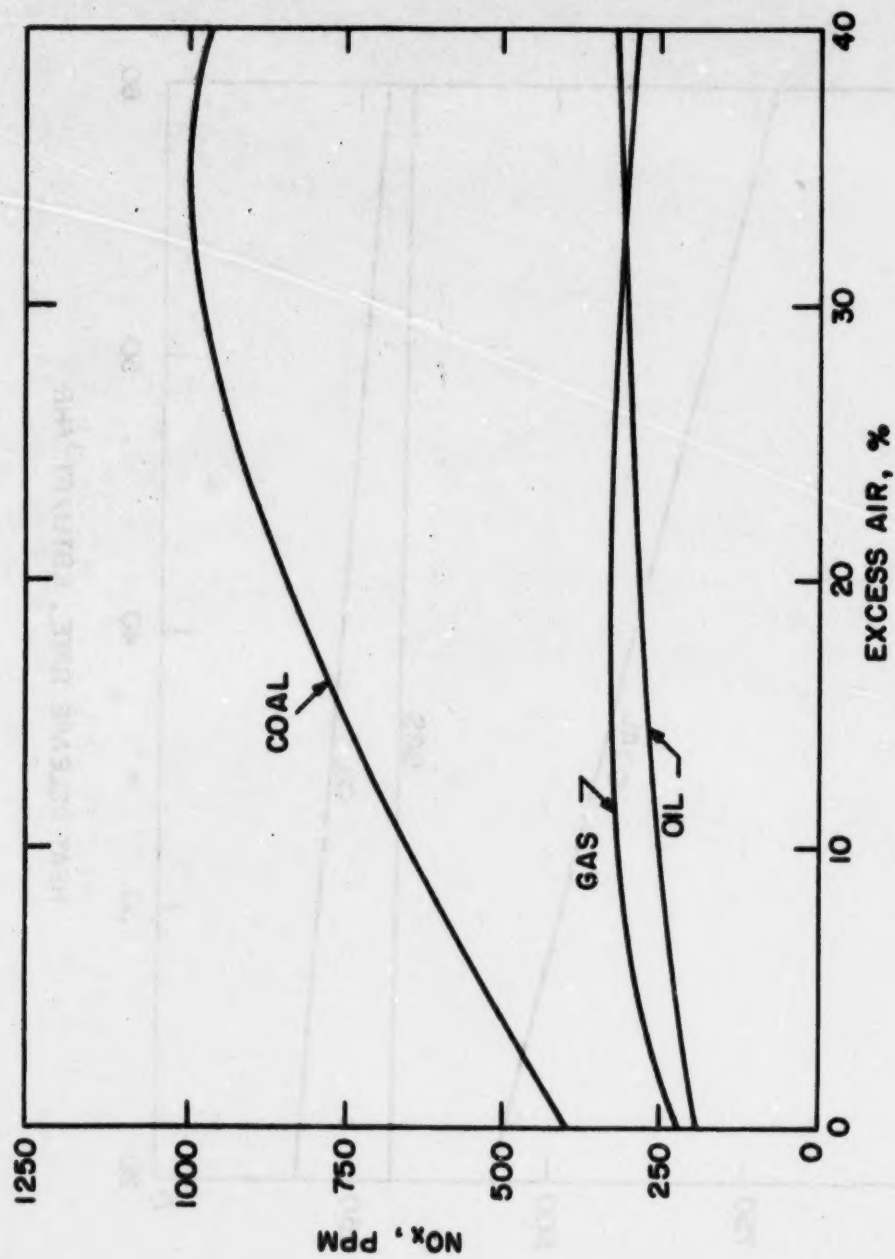


Figure 3. Effect of Excess Air on NO_x Emissions (18).

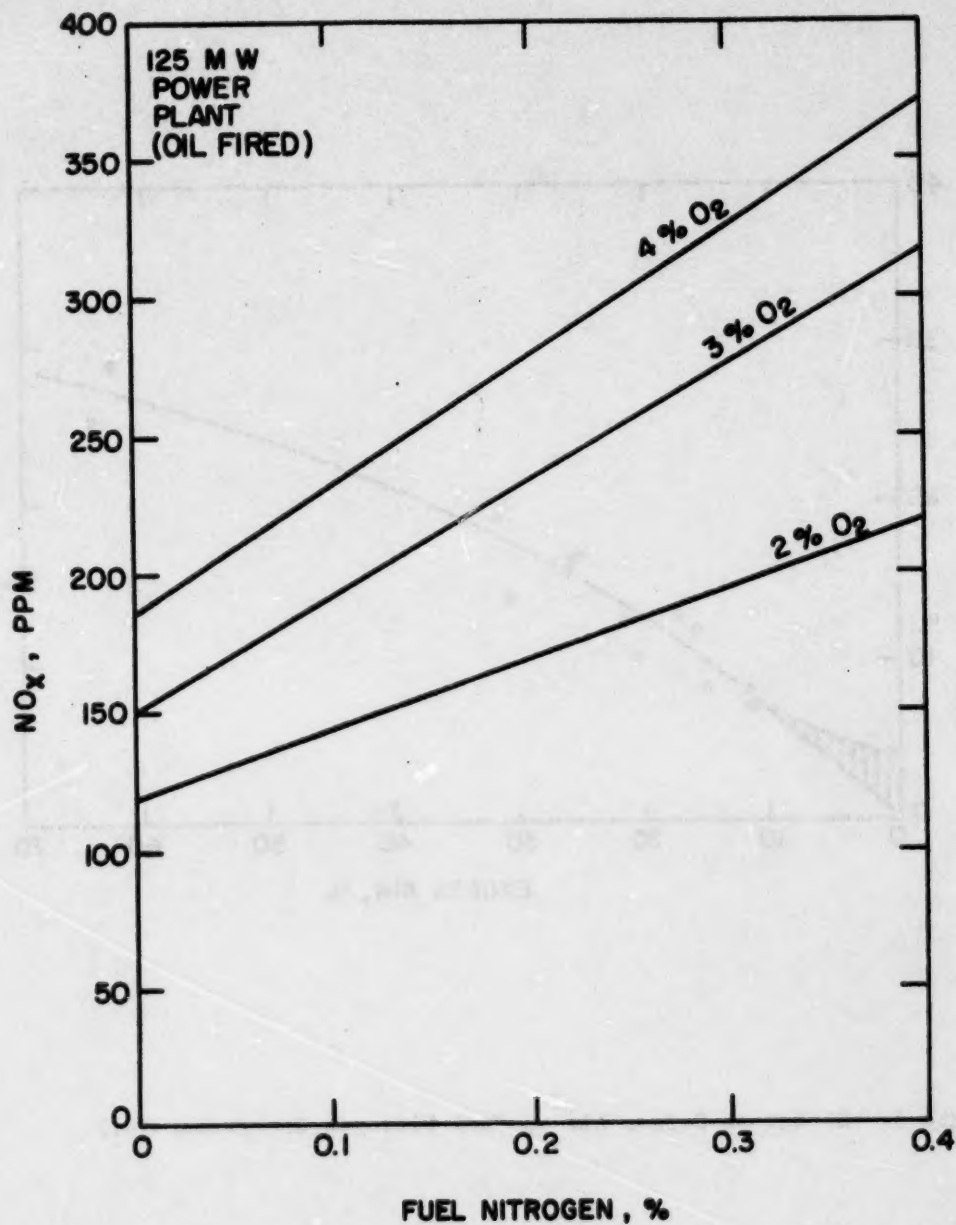


Figure 4. Effect of Fuel Nitrogen on NO_x Emissions (5).

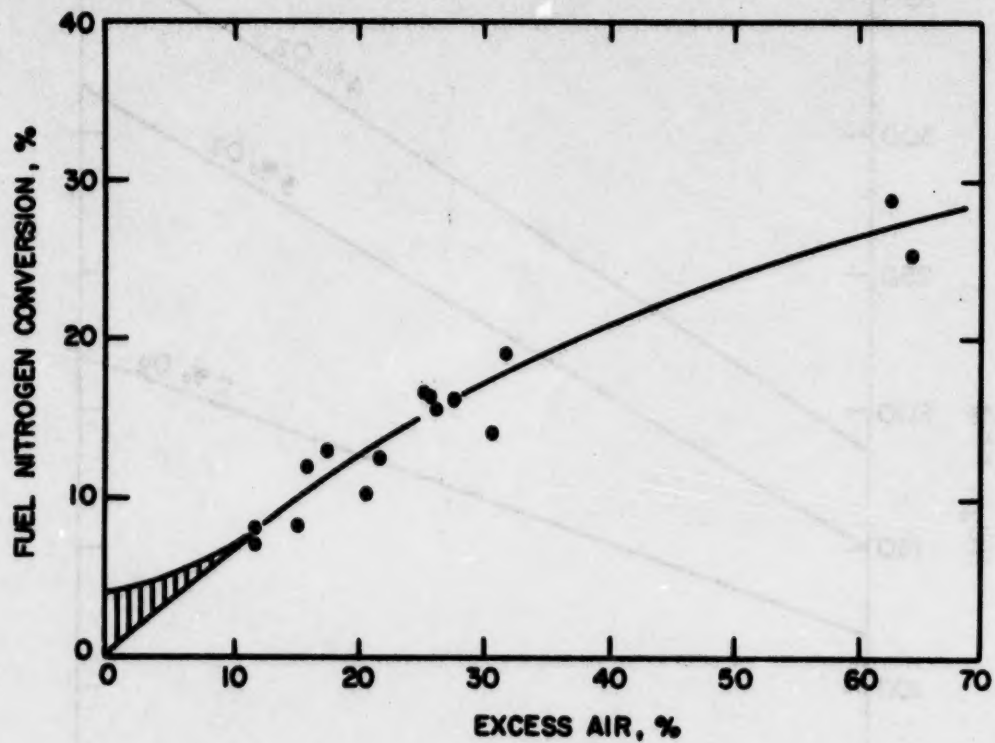


Figure 5. Effect of Excess Air on Fuel Nitrogen Conversion (47).

The flue gas from fossil-fueled boilers contains several other pollutants in addition to NO_x . Although most of the processes under consideration were tested on either gas- or oil-fired flue gas, several of these pollutants, particularly hydrogen chloride (HCl), sulfur oxides (SO_x), and particulates, will have significant impacts on the operation of these NO_x processes when they are adapted for use on coal-fired boilers. A comparison of typical flue gas compositions from both oil- and coal-fired boilers is presented in Table 7. Concentrations of these pollutants are shown to be larger for coal firing as compared to oil firing.

TABLE 7. TYPICAL FLUE GAS COMPOSITIONS FROM OIL- AND COAL-FIRED 500-MW BOILERS

Component, vol %	Fossil fuel type	
	Oil ^a	Coal ^b
N_2	73.60	73.76
O_2	2.54	4.83
CO_2	11.96	12.31
SO_2	0.13	0.24
SO_3	0.0013	0.0024
NO_x	0.02	0.06
HCl	-	0.01
H_2O	11.75	8.79
Particulates (dry basis), gr/sft ³ (60°F)	0.36	6.65

a. No. 6 fuel oil: 144,000 Btu/gal, 2.5% S, 0.1% ash.

b. Coal: 10,500 Btu/lb, 3.5% S, 16% ash, 0.15% Cl; 95% S in coal is converted to SO_x in flue gas.

Of these other pollutants, the increase in HCl and particulates are probably the most important factors to consider in switching these NO_x removal processes from oil to coal. The dry processes, since in general they use catalytic reactors, are particularly sensitive to dust and plugging and the catalyst base material may be subject to chemical attack. The flue gas from a typical coal-fired boiler (10,500 Btu/lb, 16% ash, 500 MW) contains about 20 times as much dust as an oil-fired boiler of the same size. Hence, operating problems and equipment modifications in the reductor section can be expected due to the increased particulate levels. These particulates from a coal-fired boiler have the typical chemical composition given in Table 8 and a particle size range of up to 21.5 μ .

TABLE 8. CHEMICAL COMPOSITION OF FLYASH FROM A COAL-FIRED BOILER (37)

Component	Range of concentration, % by wt
Silica (SiO_2)	38-58
Alumina (Al_2O_3)	20-40
Iron oxide (Fe_2O_3)	6-16
Lime (CaO)	2-10
Magnesia (MgO)	1-3.5
Potash (K_2O)	2-5.5
Sulfuric anhydride (SO_3)	0.5-2.5

WET NO_x REMOVAL PROCESSES

INTRODUCTION TO THE WET FLUE GAS DENITRIFICATION PROCESSES

The wet flue gas denitrification processes were, in most cases, designed to take advantage of technology already available from the previously developed flue gas desulfurization (FGD) systems. Except for the absorption-oxidation processes (defined below), the wet processes were all originally designed as simultaneous SO₂-NO_x removal systems. The absorption-oxidation processes were originally developed for the treatment of tail gases from nitric acid (HNO₃) plants and probably, due to the process chemistry, can economically be used for NO_x removal only.

The NO_x formed during the combustion of coal is present in the flue gas mainly in the form of NO (90-95% of the total NO_x) with the remainder being essentially NO₂. Unfortunately NO is relatively insoluble in aqueous solution and thus presents a formidable obstacle for these wet NO_x removal processes. NO₂, on the other hand, although not nearly as soluble in aqueous solution as SO₂, is much more soluble than NO (see Relative Solubilities of Various Gases in Appendix B). The main problem associated with any wet NO_x removal process is to force the NO_x, particularly the NO, which is present in relatively low concentrations in the flue gas (600 ppm) into the scrubbing solution where the NO_x can be concentrated and more economically converted into other forms.

The two common methods of removing the NO_x from the inlet flue gas are: dissolving the NO_x in the absorbing solution without pretreating them or using a gas-phase oxidant to convert the relatively insoluble NO, either partially or entirely, to NO₂. Thus, the wet flue gas denitrification processes can be divided into two major classes, absorption or oxidation, depending on whether or not the inlet flue gas is treated with a gas-phase oxidant.

Each of these major classes are further subdivided into two subsections based on the further treatment of the absorbed NO_x in the scrubbing solution. One subsection in each of the two major classes includes those processes which reduce the absorbed NO_x, either partially or entirely, to molecular N₂ or ammonia (NH₃)-type compounds. The other subsection includes all the other processes in the class which do not reduce the absorbed NO_x. Thus each of the wet NO_x processes can be listed under one of the following groups: oxidation-absorption-reduction, oxidation-absorption, absorption-reduction, or absorption-oxidation. Figure 6 graphically shows this classification system. For example, the Moretana Calcium process first oxidizes the NO_x with chlorine dioxide (ClO₂) (oxidation step) and once the NO_x is absorbed into the scrubbing solution (absorption step), it is reduced to molecular N₂ and NH₃.

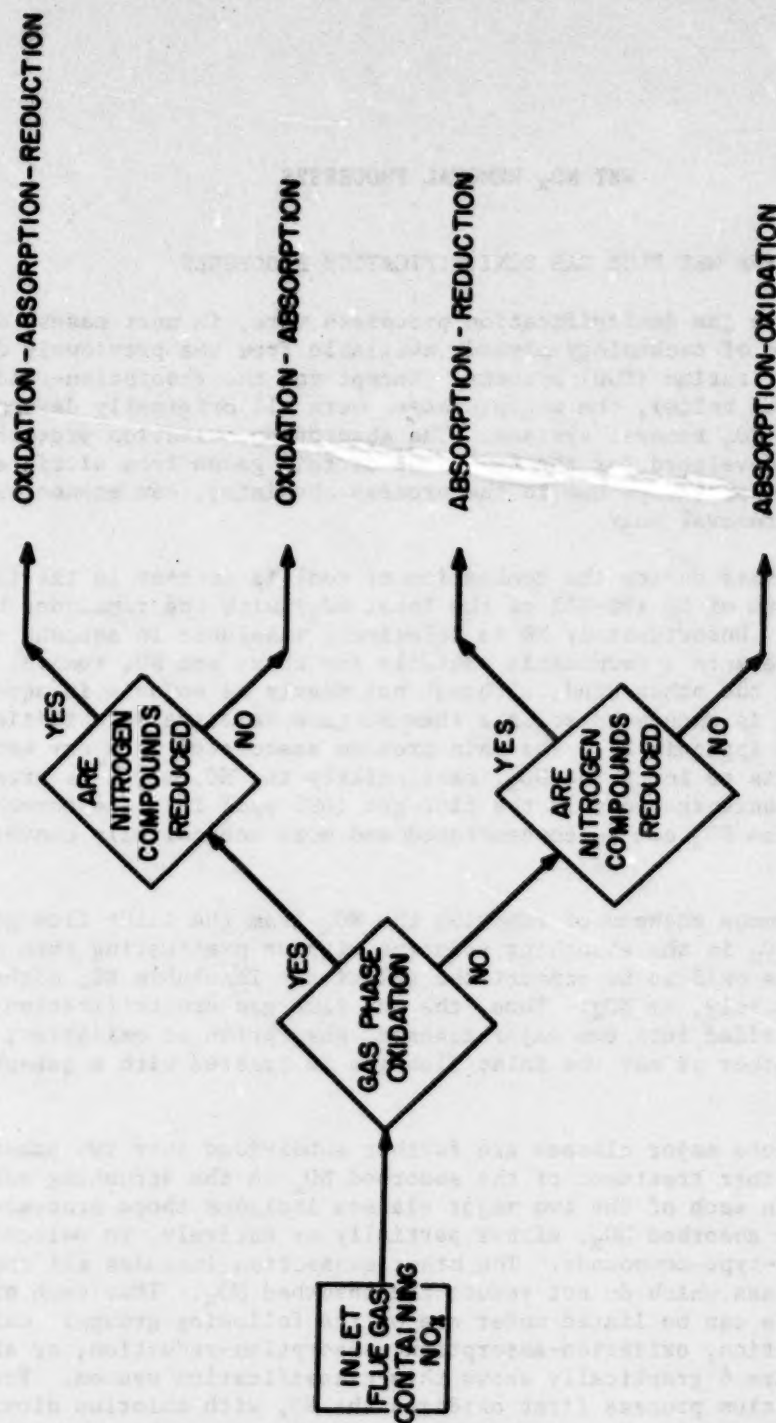


Figure 6. Classification System for Wet NO_x Removal Processes.

compounds (reduction step). Thus the Moretana Calcium process would be listed as a wet, oxidation-absorption-reduction process.

Each of these four types of wet flue gas denitrification processes is explained in greater detail in this section under separate headings. Each of the flue gas denitrification processes included in this study is listed under the specific subsection in which they belong. A detailed discussion of each of these wet processes is given later in this section. A general comparison of various operating parameters for each type of wet process is shown in Table 9.

Absorption-Oxidation Processes

The absorption-oxidation processes were originally developed to treat the tail gas from HNO_3 plants and later were adapted for FGT. These processes absorb the relatively insoluble NO into an aqueous salt solution containing a liquid-phase oxidizing agent. This oxidizing agent rapidly converts the absorbed NO_x into nitrate (NO_3^-) salts which then must be removed from a wastewater stream.

These absorption-oxidation processes have two fundamental problems inherent to their basic process chemistry. The most critical problem is that the liquid-phase oxidizing agent not only oxidizes the absorbed NO but also readily oxidizes any absorbed SO_2 . Thus for flue gas denitrification applications, the SO_2 must be removed in a separate absorber prior to entering the denitrification section to prevent the excess consumption of the oxidizing agent. These absorption-oxidation processes are not simultaneous SO_2 - NO_x removal processes but are simply the second stage of a two-stage processing scheme--one stage for SO_2 removal and a second for denitrification.

The second fundamental problem is that these processes rely on absorbing relatively insoluble NO into an aqueous salt solution. Although the absorption-reduction processes, in which the reactions are catalyzed, have a similar problem, the absorption of the NO is even more difficult in the absorption-oxidation processes which do not use catalysts since the catalyst activity would be destroyed by the liquid-phase oxidant. For this reason the absorber for removing the NO_x will be large with a high liquid to gas (L/G) ratio.

The three processes included in this study which are examples of this type of denitrification scheme are the Mon Alkali Permanganate process, the Nissan Permanganate process, and the original Kobe Steel wet process. The development of the latter, the Kobe Steel process using calcium hypochlorite [$\text{Ca}(\text{ClO})_2$] has recently been terminated (43). One other absorption-oxidation process, the Hodogaya process, has been reported (5) to be undergoing development but no information has been made available.

A list of the advantages and disadvantages common to all of the absorption-oxidation processes is given in Table 10.

TABLE 9. COMPARISON OF WET NO_x REMOVAL PROCESSES

Process characteristics ^a	Wet NO _x removal process type			
	Absorption-oxidation	Oxidation-absorption	Oxidation-absorption-reduction	Absorption-reduction
Simultaneous SO ₂ -NO _x removal	-	x ^b	x	x
Achieves high SO ₂ removal (>95%)	-	x	x	x
Achieves moderate NO _x removal (>85%)	x	x	x	-
Operating conditions				
Requires absorption catalyst	-	-	x ^b	x
Requires liquid-phase oxidant	x	-	-	-
Requires gas-phase oxidant	-	x	x	-
Requires large absorber	x	x	-	x
Requires flue gas reheat	x	x	x	x
Forms nitrate salts in wastewater	x	x	x ^b	-
Requires specific range of flue gas constituents	x	-	x ^b	x
Current development status				
Tested on coal-fired flue gas	-	x ^b	-	x ^b
Tested on pilot plant or larger scale	-	x	x	x ^b

a. An "X" indicates the process has this characteristic.

b. Depends on process.

TABLE 10. ADVANTAGES AND DISADVANTAGES OF ABSORPTION-OXIDATION PROCESSES

Advantage	Disadvantage
Achieves high NO_x removal efficiency	Requires two separate absorbers—one for desulfurization and one for denitrification
	Requires liquid-phase oxidizing agent
	Requires exceedingly large denitrification absorber and high absorber L/G
	Converts absorbed NO_x to wastewater NO_3^- salts
	Requires flue gas reheat

Oxidation-Absorption Processes

The oxidation-absorption processes are a catch-all group which includes all of the other oxidation processes which do not meet the criteria for inclusion in the oxidation-absorption-reduction section. Thus an overview of oxidation-absorption processes with generalized advantages and disadvantages is rather difficult. There are, however, two types of oxidation-absorption processes at the present time: (1) equimolar NO - NO_2 absorption and (2) NO_2 or N_2O_5 absorption. Although both of these types of processes result in a byproduct NO_3^- solution, the overall processes are substantially different.

The equimolar absorption processes such as those developed by Kawasaki Heavy Industries and Ube Industries are based on the absorption of N_2O_3 which is formed by the gas-phase reaction of NO and NO_2 . Unfortunately the NO_x in power plant stack gas is mostly NO (>90%) and a NO_2 -rich recycle stream must be added to the flue gas to adjust the molar ratio of NO_2 and NO to one. The source of this NO_2 -rich recycle stream for the Ube Industries wet process has not been identified, but in the Kawasaki process the nitrite (NO_2^-) salts formed during the absorption of N_2O_3 are chemically decomposed into an NO -rich gas stream and NO_3^- salts. This NO -rich stream is then air oxidized to NO_2 and reinjected into the flue gas prior to the absorber. Thus for every 2 mols of NO_x absorbed, i.e., 1 mol of NO and 1 mol of NO_2 , 1 mol of NO_3^- salt is formed and 1 mol of NO is regenerated, oxidized to NO_2 , and reinjected into the flue gas for reabsorption.

This equimolar absorption mechanism is complicated by the fact that when the NO_x concentration in the flue gas falls below approximately 200 ppm, the rate of formation and hence absorption of N_2O_3 rapidly decreases to insignificant levels. For 80-90% NO_x removal the flue gas must be further treated in another stage with a gas-phase oxidant to convert all the remaining

NO_x to NO_2 prior to absorption. Although the use of an NO_2 -rich recycle stream, at least for coal-fired boilers, substantially reduces the consumption of expensive ozone (O_3), the generation of this NO_2 -rich stream further complicates an already complex process.

The oxidation-absorption processes based on NO_2 or N_2O_5 absorption are apparently earlier versions of the present day oxidation-absorption-reduction systems. The only example of this class of oxidation-absorption process included in this review is the Tokyo Electric-Mitsubishi Heavy Industries (MHI) process. The NO_x in the flue gas is converted to N_2O_5 using an excess of O_3 . The O_3 requirement, for the same inlet NO_x concentration, is 50% higher for the Tokyo Electric-MHI process than for the other oxidation processes using O_3 . The resulting N_2O_5 forms HNO_3 when absorbed into aqueous solution and is removed and concentrated to form a 60% HNO_3 solution as byproduct. This desire to form only byproduct HNO_3 and eliminate the need to treat NO_3^- wastewater streams means that this process is limited to clean flue gas (no dust or SO_x). The high O_3 consumption rate is also a significant disadvantage for this type of oxidation-absorption processes. For these reasons the Tokyo Electric-MHI system is not expected to have a major role in reducing the NO_x emissions from power plants in the U.S.

The advantages and disadvantages common to this form of flue gas denitrification are shown in Table 11. It should be pointed out that although Table 11 lists only a very few advantages and disadvantages, this is the result of grouping two significantly different flue gas denitrification processes under one broad heading and does not necessarily connote a desirable type of NO_x removal process. More specific advantages and disadvantages are listed in the detailed discussion of each process.

TABLE 11. ADVANTAGES AND DISADVANTAGES OF OXIDATION-ABSORPTION PROCESSES

Advantage	Disadvantage
Achieves high NO_x removal efficiency (85-90%)	Requires expensive gas-phase oxidant
	Converts some of the absorbed NO_x to NO_3^-
	Requires flue gas reheat

Oxidation-Absorption-Reduction Processes

The oxidation-absorption-reduction processes are simply modifications of each company's original FGD system and were specifically developed for simultaneous SO_2 - NO_x removal from power plant flue gas. These processes are based on using a gas-phase oxidant to convert all of the NO_x to NO_2 which is

much more soluble in aqueous solution than NO. Before entering the absorber the flue gas is injected with a gas-phase oxidizing agent, either O_3 or ClO_2 , to convert the NO to NO_2 .

This gas-phase oxidant rapidly and selectively oxidizes the NO and the resulting NO_2 is absorbed into the aqueous sulfite (SO_3^{2-}) solution. The SO_2 in the flue gas is simultaneously absorbed and forms either the SO_3^{2-} or bisulfite (HSO_3^-) ion in the scrubbing solution. These SO_3^{2-} ions are partially oxidized to sulfate (SO_4^{2-}) during the reduction of the absorbed NO_x and the remaining SO_3^{2-} is oxidized by air to SO_4^{2-} in the regeneration section and removed as gypsum ($CaSO_4 \cdot 2H_2O$). The absorbed NO_x is at least partially reduced and removed as a combination of NO_3^- salts, molecular N_2 , and NH_3 -based waste stream.

The degree of reduction of the NO_x depends on whether a catalyst is present in the scrubbing solution to aid in the absorption of the NO_x . The Chiyoda Thoroughbred 102 process, which uses a weak sulfuric acid (H_2SO_4) solution, and the Moretana Sodium process do not use a catalyst for NO_2 absorption and approximately half of the absorbed NO_x is reduced to molecular N_2 and the other half is converted to NO_3^- salts. The remaining oxidation-absorption-reduction processes are based on limestone slurry scrubbing with a proprietary catalyst added to the scrubbing solution to enhance NO_x absorption. The addition of this catalyst apparently results in most of the NO_x being reduced to complex N-S compounds such as sulfamine $[NH(SO_3)_2]^-$ salts. Only relatively minor amounts of molecular N_2 and NO_3^- salts are formed in these processes. These complex N-S compounds are then decomposed into various NH_3 -based byproducts depending on the process involved.

The use of a gas-phase oxidant decreases the size of the absorber and lowers the absorber L/G ratio since NO_2 is relatively soluble in aqueous solution. However, its use is also the major drawback for these processes since both O_3 and ClO_2 are expensive and must be generated onsite. The use of ClO_2 also leads to high levels of chlorides (Cl^-) in the circulating solution and the resulting production of Cl^- salts in the wastewater. A brief description of the technical and economic considerations involved in generating O_3 or ClO_2 is included in Appendix A.

The examples of oxidation-absorption-reduction processes considered in this study include the Chiyoda Thoroughbred 102, the Moretana Sodium, the Moretana Calcium, the Ishikawajima-Harima Heavy Industries, and the MHI. Additional oxidation-absorption-reduction processes have been reported by others (5), but are not detailed in this study due to lack of available information. These processes include those undergoing development by Osaka Soda and Shirogane in Japan.

A list of the general advantages and disadvantages for oxidation-absorption-reduction processes is given in Table 12. Table 13 gives a simplified comparison of each of these oxidation-absorption-reduction processes.

TABLE 12. ADVANTAGES AND DISADVANTAGES OF
OXIDATION-ABSORPTION-REDUCTION PROCESSES

Advantage	Disadvantage
Removes NO _x and SO ₂ simultaneously	Requires an expensive gas-phase oxidant
Produces a potentially marketable byproduct (CaSO ₄ ·2H ₂ O)	Forms an N-containing waste stream
Achieves high NO _x removal rates (85-90%)	Requires flue gas reheat
Achieves high SO ₂ removal rates (80-90%)	

Absorption-Reduction Processes

The absorption-reduction processes were apparently specifically developed for the simultaneous removal of SO₂ and NO_x from power plant flue gas without using an expensive gas-phase oxidant. These processes are based on certain ferrous (Fe⁺²) chelating compounds which "catalyze" the absorption of the relatively insoluble NO. Thus, the need for an expensive gas-phase oxidant is eliminated. The NO is absorbed into the scrubbing solution and forms a complex with the chelated compound. The SO₂ is simultaneously absorbed into the scrubbing solution as the SO₃⁻ ion and reacts with the NO complex. The NO is reduced to molecular N₂, the Fe⁺² chelating compound is regenerated, and the SO₃⁻ ion is oxidized to SO₄⁻ in a single reaction. This SO₄⁻ ion is generally removed as CaSO₄·2H₂O, but in one specific case the SO₄⁻ is removed as ammonium sulfate [(NH₄)₂SO₄].

The absorption of NO requires a large absorber and a high L/G ratio in the absorber since even with the use of the catalyst, NO is relatively insoluble in the scrubbing solution. Due to the basic chemistry of these absorption-reduction processes, they are sensitive to the inlet flue gas composition, particularly the levels of O₂, SO₂, and NO_x. The molar ratio of SO₂ to NO_x in the flue gas must remain above approximately 2.5 for good denitrification efficiency and the flue gas O₂ must remain as low as possible. As the flue gas O₂ level increases and/or the mol ratio of SO₂ to NO_x decreases, the NO_x removal efficiency will decline.

The examples of reduction processes being considered in this study include the Asahi Chemical, the Chisso, the Mitsui wet, the Kureha wet, and the Pittsburgh Environmental and Energy Systems.

A list of the advantages and disadvantages common to all of the absorption-reduction processes is given in Table 14 and a simplified comparison of each of these absorption-reduction processes is given in Table 15.

TABLE 13. COMPARISON OF OXIDATION-ABSORPTION-REDUCTION PROCESSES

	Chiyoda Thoroughbred 102	Ishikawajima-Harima Heavy Industries	Mitsubishi Heavy Industries	Moretana Calcium	Moretana Sodium
Development status, MW	Bench scale (0.3)	Pilot plant (1.6)	Pilot plant (0.6)	Prototype (8.3)	Prototype (10-40)
SO ₂ removal, %	95	90+	95+	95+	95+
NO _x removal, % (inlet NO _x level)	80 (150 ppm)	80 (180 ppm)	80-90 (150 ppm)	90 (200 ppm)	90 (200 ppm)
Longest continuous operation	-	3000 hr	720 hr	-	Normal plant availability
Absorbent raw material (catalyst)	H ₂ SO ₄ /Fe ₂ (SO ₄) ₃ /a	CaCO ₃ (CuCl ₂ , NaCl)	CaCO ₃ (unknown)	CaCO ₃ (CuCl ₂ , proprietary additive)	NaOH
Oxidant (oxidant:NO _x ratio)	O ₃ (1.5)	O ₃ (1.0)	O ₃ (1.0)	ClO ₂ (0.55)	ClO ₂ (0.55)
Byproducts	N ₂ , CaSO ₄ ·2H ₂ O	N ₂ , CaSO ₄ ·2H ₂ O	NH ₃ , CaSO ₄ ·2H ₂ O	N ₂ , CaSO ₄ ·2H ₂ O	N ₂ , Na ₂ SO ₄
Waste disposal (other than gypsum)	-	CaSO ₄ -CuCl ₂ -NaCl	10-15% NH ₃ gas	CaCl ₂ -Ca(NO ₃) ₂ (aq)	Na ₂ SO ₄ , NaCl
Absorber L/G ratio	-	62-75	43-62	20-45	25
Reported capital investment, b \$/kW	107	84	-	-	134
Reported revenue requirements, b mills/kWh	6.73	6.80	-	-	8.94
Unusual features or unique problems	Reactor-crystallizer Biological denitrification	Thermal decomposer	Thermal decomposer	"Moretana" absorber	"Moretana" absorber Evaporation of wastewater

a. Oxidation catalyst.

b. 1976 dollars except for Chiyoda which are for 1977; for source of value see detailed process description.

TABLE 14. ADVANTAGES AND DISADVANTAGES OF THE
ABSORPTION-REDUCTION PROCESSES

Advantage	Disadvantage
Removes SO ₂ and NO _x simultaneously	Requires a large absorber and a high L/G ratio in the absorber
Produces a potentially marketable byproduct (CaSO ₄ ·2H ₂ O)	Requires flue gas reheat
Achieves a high SO ₂ removal efficiency (>90%)	Involves a series of complicated processing steps
	Requires specific range of flue gas constituents

TABLE 15. COMPARISON OF ABSORPTION-REDUCTION PROCESSES

	Asahi Chemical	Chisso	Kureha	Mitsui	PENNY SCORE
Development status, MW	Bench scale (0.02)	Bench scale (0.1)	Pilot plant (1.6)	Bench scale (0.05)	Pilot plant (1.0)
SO ₂ removal, %	95+	95+	95+	95+	90
NO _x removal, % (inlet NO _x level)	80-85 (150-250 ppm)	70-80 (200 ppm)	80-85 (200 ppm)	85	60 (400-900 ppm)
Longest continuous operation	1000 hr	335 hr	3000 hr	-	52 hr
Absorbent raw material (catalyst)	Na ₂ CO ₃ (Fe ²⁺ -EDTA)	NH ₃ (proprietary)	Acetic acid (proprietary)	-	FeS
Byproducts	N ₂ , CaSO ₄ ·2H ₂ O	(NH ₃) ₂ SO ₄ (aq)	N ₂ , CaSO ₄ ·2H ₂ O	(proprietary) N ₂ , concentrated SO ₂	N ₂ , S
Waste disposal (other than gypsum)	Some CaSO ₃ ·1/2H ₂ O	Fe(OH) ₂ -ash sludge	-	-	FeS-ash sludge
Absorber L/G ratio	"Trace" Ca(NO ₃) ₂ (aq) 90-100	90-100	125-185	-	10-15
Reported capital investment, \$/kW	127	98	65	-	125
Reported revenue requirements, \$/kW	7.4	6.6	4.8	-	0.49
Unusual features or unique problems	Extremely large absorber Extensive solid handling	Extremely large absorber Possibility of sulfidic plume	Extremely large absorber Possibility of NH ₃ emissions	Extremely large absorber Electrolytic reduction of Fe ³⁺	Coal-fired reducing kiln Extensive solids handling

a. 1977 dollars except for Chisso which are 1976; for source of value see detailed process description.

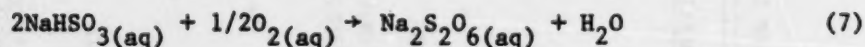
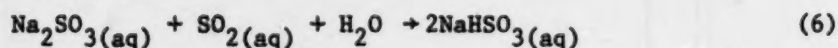
ASAHI CHEMICAL PROCESS - WET, ABSORPTION-REDUCTION ($\text{NO}_x\text{-SO}_x$)

Process Description and Principles of Operation (107)

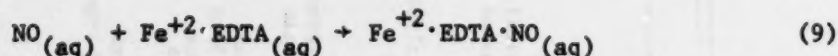
This process developed by the Asahi Chemical Industry Company uses an alkali solution (Na_2SO_3) to absorb both SO_2 and NO_x . Since NO_x is relatively insoluble in aqueous solutions, an Fe^{+2} chelating compound has been added to catalyze the absorption of NO_x . The five major sections of this system include (1) prescrubbing, (2) absorption of both SO_2 and NO_x , (3) reduction of NO_x , (4) decomposition of dithionate ($\text{S}_2\text{O}_6^{--}$), and (5) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production. The Asahi flue gas denitrification system, as a whole, is an intricate processing scheme made up of many simple processing units as shown in the block flow diagram in Figure 7.

The flue gas from the air heater passes through a prescrubber which is expected to remove 99% of both the particulates and the HCl resulting from the coal combustion. In addition, some of the circulating solution evaporates to adiabatically cool and humidify the flue gas from 150°C (300°F) to 53°C (127°F). The liquid effluent from the particulate scrubber drops to a holding tank from which most of the liquid is recirculated to the prescrubber after fresh makeup H_2O has been added. A small purge stream is removed and pumped to a flyash thickener. The thickener overflow stream is recycled to the effluent holding tank. The thickener bottoms containing the flyash and the Cl^- are removed, neutralized by limestone, and pumped to a waste disposal pond. Thus, the flyash and Cl^- in the flue gas are removed and treated before the flue gas reaches the absorber.

After leaving the prescrubber the flue gas enters a sieve tray absorber where it flows countercurrently to a mixed Na salt scrubbing solution containing $\text{Fe}^{+2}\cdot\text{EDTA}$ (ethylene diamine tetraacetic acid) at a pH of 6.3. As the flue gas passes through the lower portion of the absorber, the SO_2 is rapidly absorbed into the solution and undergoes the following reactions.



The NO_x on the other hand is gradually absorbed over the entire absorber and reacts according to the following equation to form an Fe^{+2} chelate complex.



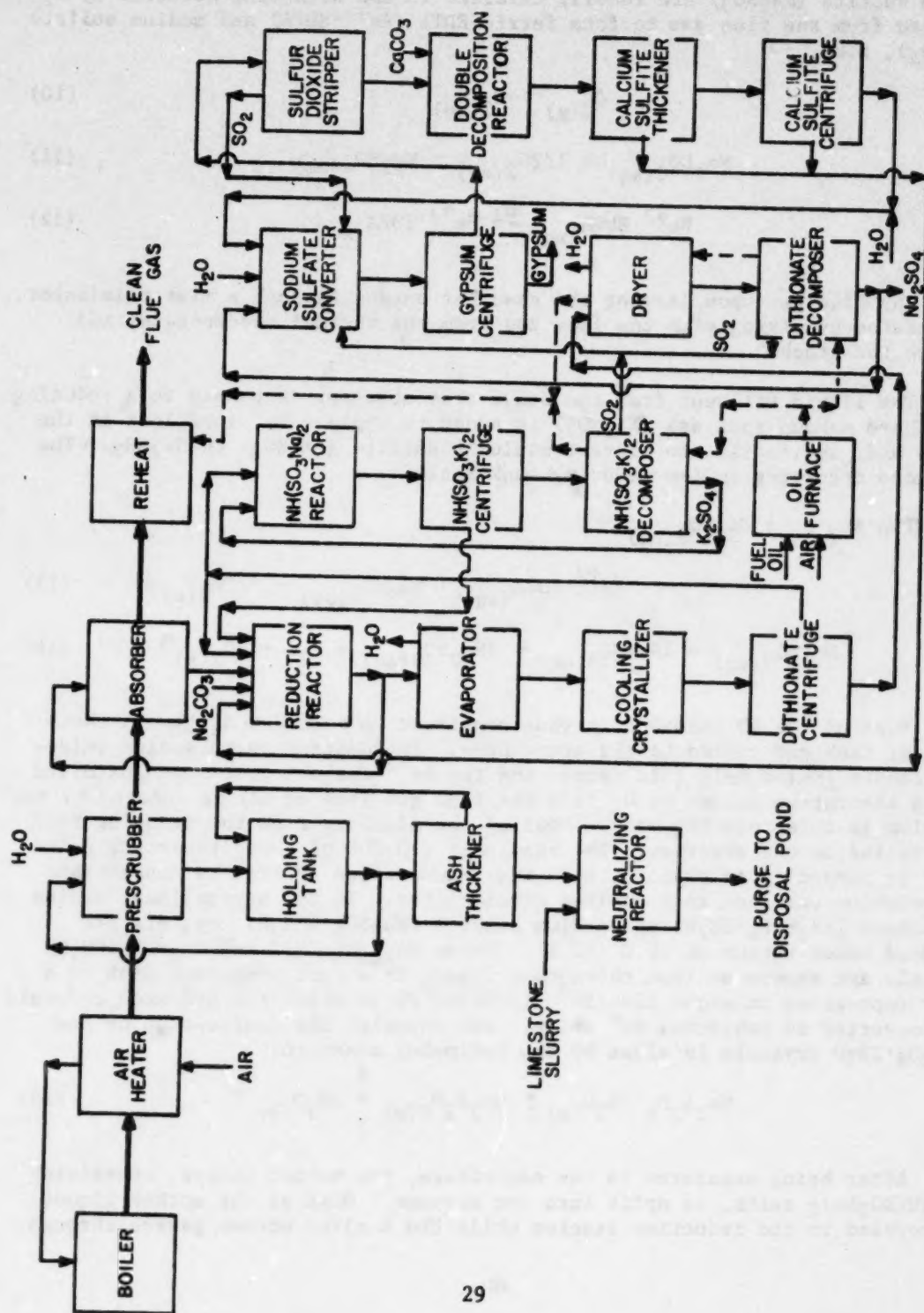
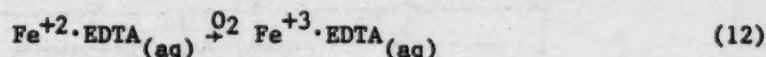
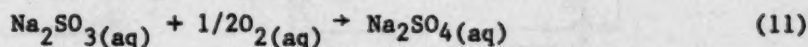
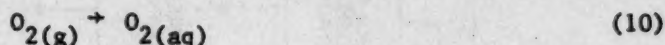


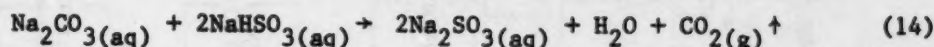
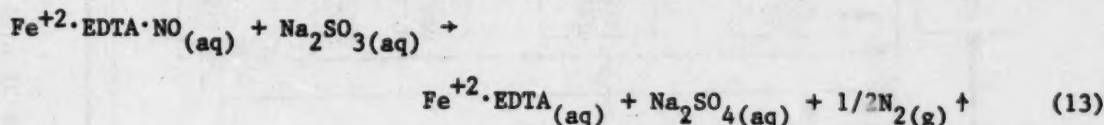
Figure 7. Flow Diagram of Asahi Chemical Process.

In addition to these primary reactions, other side reactions are occurring simultaneously in the absorber. Both the Fe^{+2} chelating compound and the sodium sulfite (Na_2SO_3) are readily oxidized in the scrubbing solution by O_2 absorbed from the flue gas to form ferric EDTA ($\text{Fe}^{+3}\cdot\text{EDTA}$) and sodium sulfate (Na_2SO_4), i.e.,

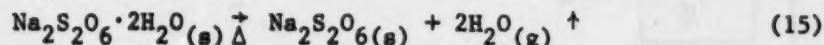


The flue gas upon leaving the absorber passes through a mist eliminator, is reheated by mixing with the flue gas from the thermal decomposers, and sent to the stack.

The liquid effluent from the sieve tray absorber is pumped to a reducing tank where makeup soda ash (Na_2CO_3) is added to replace Na^+ ions lost in the system and, indirectly, to convert sodium bisulfite (NaHSO_3) to Na_2SO_3 . The reactions occurring in the reducing tank include:

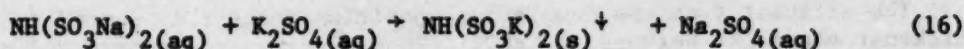


Most of the NO absorbed is thus converted to harmless N_2 gas in the reducing tank and vented to the atmosphere. In addition, some sodium imido-disulfonate $[\text{NH}(\text{SO}_3\text{Na})_2]$ is formed and the Fe^{+2} chelating compound oxidized in the absorption column by O_2 from the flue gas (see eq 12) is reduced by the SO_3^- ion in this reducing tank. Most of the effluent from the reducing tank is recycled to the absorber. The remainder (10-20% of the circulating solution) is pumped to an evaporator in the regeneration section to concentrate the solution and then to a cooling crystallizer. In the crystallizer sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_6\cdot 2\text{H}_2\text{O}$) and sodium sulfate ($\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$) crystals are produced under vacuum at 10°C (50°F). These $\text{Na}_2\text{S}_2\text{O}_6\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ crystals are separated from the mother liquor in a centrifuge and sent to a dryer (operating at about $120\text{--}150^\circ\text{C}$ ($250\text{--}300^\circ\text{F}$)) in which the hydrated crystals are converted to anhydrous Na^+ salts. For example, the desiccation of the $\text{Na}_2\text{S}_2\text{O}_6\cdot 2\text{H}_2\text{O}$ crystals is given by the following reaction.

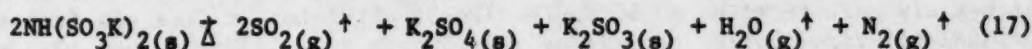


After being separated in the centrifuge, the mother liquor, containing the $\text{NH}(\text{SO}_3\text{Na})_2$ salts, is split into two streams. Most of the mother liquor is recycled to the reduction reactor while the smaller stream passes through

the $\text{NH}(\text{SO}_3\text{Na})_2$ treatment section. This section is necessary since soluble $\text{NH}(\text{SO}_3\text{Na})_2$ is formed in small quantities by a side reaction in the absorber and must be removed to prevent its buildup in the scrubbing solution. The $\text{NH}(\text{SO}_3\text{Na})_2$ is converted to insoluble potassium imidodisulfonate $\text{NH}(\text{SO}_3\text{K})_2$ by reaction with potassium sulfate (K_2SO_4).

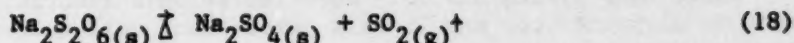


The resulting crystals of $\text{NH}(\text{SO}_3\text{K})_2$ are separated in a centrifuge and sent to a thermal cracker while the mother liquor, containing mainly dissolved Na_2SO_4 is recycled to the reducing tank. The thermal cracker, which is heated indirectly by flue gas from an oil-fired furnace, operates at 500°C (932°F) and decomposes the $\text{NH}(\text{SO}_3\text{K})_2$ into SO_2 , N_2 , and potassium sulfite (K_2SO_3) and K_2SO_4 by the following reaction.

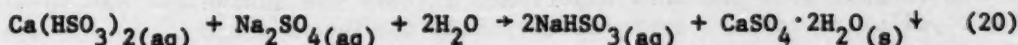
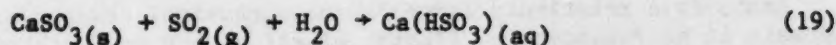


The concentrated SO_2 gas stream is sent to the Na_2SO_4 converter while the solid K_2SO_4 is recycled to the $\text{NH}(\text{SO}_3\text{Na})_2$ reactor.

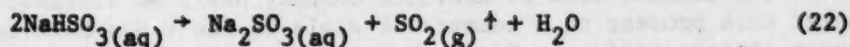
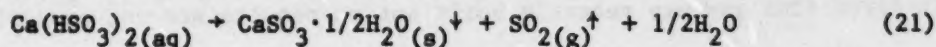
The anhydrous Na_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_6$ salt mixture from the dryer is sent to a thermal cracker where the Na^+ salt mixture is indirectly heated to 300°C (572°F) and decomposed into Na_2SO_4 and SO_2 according to the following reaction.



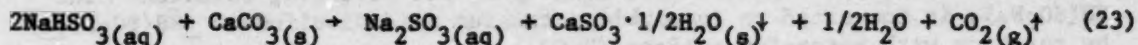
Depending on the SO_2 concentration in the flue gas, a portion of this Na_2SO_4 is removed as a byproduct, but most is sent to an Na_2SO_4 converter where it is reacted with calcium sulfite (CaSO_3) at 40°C (104°F) and a pH of 2 to produce $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The SO_2 from both the $\text{Na}_2\text{S}_2\text{O}_6$ and the $\text{NH}(\text{SO}_3\text{Na})_2$ crackers are also recycled to the Na_2SO_4 converter where the following reactions occur.



The reactor product stream is pumped to a centrifuge where $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is removed as a solid byproduct. The centrate is sent to an SO_2 stripper, operating at 95°C (203°F), pH 4, and a pressure of 100 mm Hg, where the HSO_3^- salts are partially converted to SO_3^- and SO_2 .



The SO_2 produced in the stripper is recycled back to the Na_2SO_4 converter and the effluent containing the SO_3^{2-} is sent to the double decomposition reactor where the Na_2SO_3 is converted to $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ by the following reaction with makeup calcium carbonate (CaCO_3).



The effluent from the double decomposition reactor is pumped to a thickener where the bottoms, a $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ slurry, are removed and centrifuged. The solid CaSO_3 from the centrifuge is then reslurried with makeup H_2O and recycled to the Na_2SO_4 converter. The thickener overflow and the centrate from the centrifuge, both of which are essentially Na_2SO_3 solutions, are recycled as a single stream to the absorber.

Status of Development

The Asahi process has only been tested, as an integrated system, in a bench-scale unit treating 40-60 Nm^3/hr (24-35 sft^3/min) of flue gas from a residual oil-fired boiler containing 150-200 ppm NO_x , 1250-1500 ppm SO_2 , and 3-6% O_2 . During a 1000-hr continuous test, this processing unit was able to demonstrate 80-85% removal of NO_x and more than 99% removal of SO_2 . The absorption, crystallization, and decomposition portions of this system have been confirmed and scaleup data obtained in a bench-scale unit treating 500-600 Nm^3/hr . This process has not been tested on flue gas from a coal-fired boiler.

Since this system has only been tested on a laboratory scale, the next major development step should be a pilot-plant unit in the 1-10 MW range before a prototype or commercial unit is constructed. In addition to pilot-plant testing on flue gas from an oil-fired boiler, this process should also be tested on flue gas from a coal-fired boiler to determine its ability to handle the increased particulate, Cl^- , and trace metal loadings associated with coal combustion.

Background of Process Developer

Asahi is a relatively large Japanese chemical company with its primary emphasis in petrochemicals, fibers, plastics, and basic chemicals. Asahi has had considerable previous experience in both the design and development of air pollution control systems, including the development of an FGD system for power plant stack gas and a denitrification system for HNO_3 tail gas. Their FGD process, based on a limestone slurry scrubbing solution, is being used in a commercial unit treating 500,000 Nm^3/hr (167 MW equiv) of flue gas from an oil-fired boiler. Their denitrification system for treating HNO_3 tail gas is an NH_3 -based selective catalytic reduction (SCR) process similar to the dry, NO_x -only processes. A pilot plant to test this dry process on oil-fired flue gas was recently built but no results are yet available.

At the present time no American company has been licensed by Asahi to market this process on a commercial scale in the U.S.; however, Asahi does have a liaison office in New York City through which inquiries about this

process are handled. Asahi has recently entered into a formal agreement with the NUS Corporation, an engineering and environmental consulting firm in Rockville, Maryland, to advance the Asahi process through the pilot and prototype stages on coal-fired flue gas in the U.S.

Published Economic Data

The published economics for this process should be considered as only tentative, and subject to revision, since the entire process system is in an early stage of development and has not been tested as an integrated unit in a pilot plant. Asahi estimates (107) the total capital investment (construction basis: U.S. and mid-1977 costs) for a system using their process to treat flue gas from a 500-MW coal-fired unit containing 2200 ppm SO₂ and 600 ppm NO_x to be \$63.6 million (\$127/kW). The estimated revenue requirement for this simultaneous SO₂-NO_x system on the same basis is about 7.4 mills/kWh.

Raw Materials, Energy, and Operation Requirements

The raw material requirements given below are based on treating the flue gas from a 500-MW coal-fired boiler containing 2200 ppm SO₂ and 600 ppm NO_x.

Material	Quantity required
Limestone	127,000 tons/yr (short tons)
FeSO ₄ ·7H ₂ O	930,000 lb/yr
EDTA	930,000 lb/yr
Na ₂ CO ₃	16,500 tons/yr (short tons)

The associated utility requirements are:

Utility	Quantity required
Residual oil (cracking)	1,500 gal/hr
Steam (150 psig max)	110,000 lb/hr
Cooling water	2,000 gpm
Electricity	27,000 kW

The only byproducts produced under these assumptions would be 600 tons/day of CaSO₄·2H₂O, 70 tons/day of Na₂SO₄, and two small wastewater streams. One stream, which is purged from the S₂O₆²⁻ mother liquor for Cl⁻ control, contains sodium chloride (NaCl) and the other is the flyash disposal pond overflow.

The electrical requirements for this process using a sieve tray absorber are said to represent approximately 5% of the generating capacity of the boiler.

For the 500-MW system the operating manpower is estimated to be 19 men/day and the annual maintenance requirements are estimated to be \$2.54 million.

Technical Considerations

The Asahi process using Na_2SO_3 scrubbing is a relatively complex system involving many simple chemical processing steps. For example, there are six solid-liquid separation steps, six chemical reactors, two thermal decomposers, one crystallizer, and one dryer in the regeneration section. In addition, there will probably be at least four trains of sieve tray absorbers for each 500-MW boiler. Further complicating this process are numerous solid-handling systems and also relatively high temperature requirements. Although the process vendor envisions sufficient surge capacity to effectively decouple the various treatment areas, the overall system would still be relatively complex and the process control would probably be more difficult relative to other wet and dry processes.

Assuming that the particulate prescrubbing system is adequately designed for high Cl^- and particulate removal, this process could probably be applied to flue gas from a coal-fired boiler. The SO_2 removal efficiency will be relatively independent of the inlet gas composition. The NO_x removal efficiency, however, is a function of the flue gas O_2 and SO_2 concentrations. The SO_3^{2-} ion which is formed when the SO_2 is absorbed into the scrubbing solution is used to reduce both the absorbed NO to molecular N_2 and the Fe^{+3} ion back to the Fe^{+2} form. The SO_3^{2-} ion is also consumed by reaction with O_2 absorbed from the flue gas. Thus for flue gas containing 5% or less O_2 , approximately 2.5 mols of SO_2 are required in the flue gas for each mol of NO_x to obtain an NO_x removal efficiency of 80-85%. For each 1% increase in O_2 concentration in the flue gas above 5%, the NO_x removal efficiency will decrease 1-2% due to the increased oxidation of both Na_2SO_3 and the Fe^{+2} ion.

The relative insolubility of NO in the scrubbing solution requires a very high L/G ratio in the absorbers, on the order of 10-15 l/Nm^3 (65-100 gal/kft³) of gas (127°F) depending on the NO_x concentration in the flue gas. At an NO_x level of 600 ppm in the flue gas, the L/G ratio in the absorber will be about 15 l/Nm^3 (90-100 gal/kft³). The size of the absorbers is further increased by the low superficial gas velocity through the absorber (approximately one-third the gas velocity in a limestone desulfurization system). Thus, instead of four relatively small absorbers per 500 MW of capacity, as for conventional limestone desulfurization systems, four large scrubbers will be required for this simultaneous SO_2 - NO_x process. Asahi is now assessing the use of packed-bed absorbers to obtain better gas-liquid contact and thus decrease the size of the absorbers.

The relatively large differences in solubility of SO_2 and NO_x in the absorbing solution also lead to the unique situation in which the SO_2 is almost completely absorbed in the lower portion of the absorber and the upper part of the absorber is essentially a denitrification section. Although some recycle SO_3^{2-} is available in the upper portion of the absorber, most of the NO_x is converted in the reduction reactor. Thus relatively large quantities of the Fe^{+2} chelating compound are required to absorb and transport the NO until it can be reduced by the absorbed SO_2 in the reducing tank. Since the L/G ratio in the absorber is very high to facilitate NO_x removal, the SO_2 removal efficiency will be relatively insensitive to changes in flue gas composition.

Fortunately the equipment in the regeneration system will be much smaller than for the absorption section, since only 10-20% of the circulating solution passes through the regeneration section at any given time. In fact the equipment sizes will be the same order of magnitude as a conventional double-alkali desulfurization system since only the SO_3^- and SO_4^- pass through the regenerator system. The NO_x is reduced to molecular N_2 and passes out of the system before reaching the regeneration section.

Since this is a wet simultaneous process, this system can be retrofitted relatively easily onto power plants. The major consideration would be land areas available nearby for both siting the large numbers of equipment and disposing and/or storing the byproducts or wastes.

This process should have relatively good turndown capabilities since the system contains four scrubber trains, any combination of which could be shut down completely. However, during turndown the NO_x removal efficiency will decline at least somewhat since typically, when the boiler load is reduced, the airflow is not correspondingly decreased. Thus the flue gas will contain a higher concentration of O_2 and a lower concentration of SO_2 .

Most of the equipment and piping will be epoxy, elastomer, or flake glass-reinforced, polyester-lined carbon steel to prevent the corrosion and erosion problems associated with wetted flue gas and the circulating slurries and liquors. Exceptions will include the thermal crackers and the SO_2 stripper, which because of high temperature and/or low pH, will be constructed of 310 stainless steel. In addition the absorber and reducing tank will be made from 316 stainless steel.

Due to the high particulate and Cl^- removal in the prescrubbing section, the purging of a smaller amount of the absorber scrubbing solution to control the Cl^- , and the additional washing of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ cake, this byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is claimed to be suitable for use in the manufacture of wallboard. Its ability to displace naturally occurring $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the U.S. market is questionable and thus the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will probably be used as landfill material. Similarly the Na_2SO_4 will also probably be disposed in a landfill, although the process developer believes it also can be marketed as a byproduct.

The operation at relatively high temperatures (500°C) required in the thermal crackers is a disadvantage for this process. A portion of this heat (approximately 10-15%) is retained in the solids as sensible heat and is lost in the surge volume storage of these calcined products. The remaining heat is used in either drying the solids prior to cracking or reheating the clean flue gas from the absorber prior to exhausting the gas through the stack.

Environmental Considerations

During a continuous test using a sieve tray absorber on residual oil-fired flue gas (150-250 ppm NO_x ; 1250-1500 ppm SO_x ; and 3-6% O_2) in a bench-scale unit (0.2 MW equiv), 80-85% removal of NO_x and more than 99% removal

of SO_x were attained. Most of the NO_x is reduced to molecular N_2 with "trace" amounts converted to NO_3^- and the SO_x is converted mainly to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with some Na_2SO_4 formed.

If a market for the byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Na_2SO_4 can be found, the only waste disposal problem for this process will be the flyash- Ca^{++} salt solution from the prescrubber.

Critical Data Gaps and Poorly Understood Phenomena

At the present time no critical data gaps or poorly understood phenomena other than those being investigated by Asahi are readily apparent.

Advantages and Disadvantages

The major advantages and disadvantages of the Asahi sodium scrubbing are listed below. Other advantages and/or disadvantages may become more apparent once the process is tested on flue gas from a coal-fired boiler.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Produces a potentially marketable byproduct ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Na_2SO_4)
4. Operates with full particulate loadings (>7gr/sft³)

Disadvantages

1. Requires significant amounts of energy for the regeneration step
2. Has not been tested on coal-fired flue gas
3. Has been tested only in a bench-scale unit
4. Has not been operated for a long-term continuous period
5. Uses significant amounts of stainless steel or exotic materials for process equipment
6. Requires hot solids handling
7. Has a low superficial gas velocity in the absorber (<10 ft/sec)
8. Has a high L/G ratio in the absorber (>70 gal/kaft³)
9. Requires flue gas constituents within specific ranges for high NO_x removal
10. Requires an expensive liquid-phase catalyst

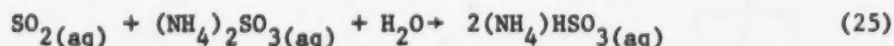
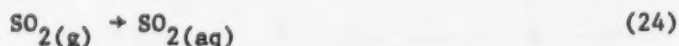
CHISSO ENGINEERING PROCESS - WET, ABSORPTION-REDUCTION (NO_x - SO_x)

Process Description and Principles of Operation (94,97)

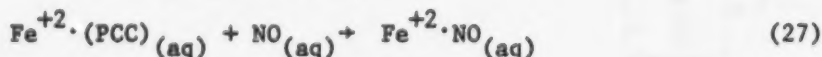
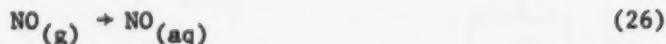
The Chisso Engineering Company's process uses an alkali solution /ammonium sulfite-- $(\text{NH}_4)_2\text{SO}_3$ / to absorb both SO_2 and NO_x . This absorption of the relatively insoluble NO_x is "catalyzed" by a proprietary Fe chelate which is added to the scrubbing solution. The Chisso process consists of four major sections including (1) prescrubbing, (2) absorption of both SO_2 and NO_x , (3) reduction of NO_x and oxidation of SO_3^{2-} , and (4) byproduct purification. The general outline of these processing sections can be seen in the block flow diagram for the Chisso process given in Figure 8. One major difference between the Chisso process and the other absorption-reduction processes is that Chisso reduces this NO_x to the ammonium (NH_4^+) ion instead of molecular N_2 and thus forms $(\text{NH}_4)_2\text{SO}_4$ as a potentially marketable byproduct.

The flue gas from the air heater at approximately 150°C (300°F) is passed through a prescrubber in which most of the particulates and Cl^- are removed. As the flue gas passes through the prescrubber it is also adiabatically cooled to approximately 53°C (127°F) and humidified by the evaporation of H_2O from the scrubbing solution. The scrubbing solution drops to a holding tank from which most of the solution is recirculated through the prescrubber. A small stream is removed and pumped to a flyash centrifuge where the flyash is separated and purged from the system. The centrate is recycled to the holding tank with a small portion removed and purged from the solution to prevent the buildup of Cl^- and trace elements in the prescrubbing solution.

After leaving the prescrubber the humidified flue gas enters the main section of the tray absorber and flows countercurrently to an $(\text{NH}_4)_2\text{SO}_3\text{-Fe}^{+2}$ chelate solution at a pH of 6-7. As the flue gas passes through the lower portion of the absorber, the SO_2 , which is much more soluble than the NO_x , is rapidly absorbed into the scrubbing solution and undergoes the following reactions.



The NO_x , particularly NO , is much less soluble in the scrubbing solution and hence is gradually absorbed over the length of the absorber. Once absorbed, the NO_x reacts to form an Fe^{+2} chelating complex,



where (PCC) denotes the proprietary chelating agent.

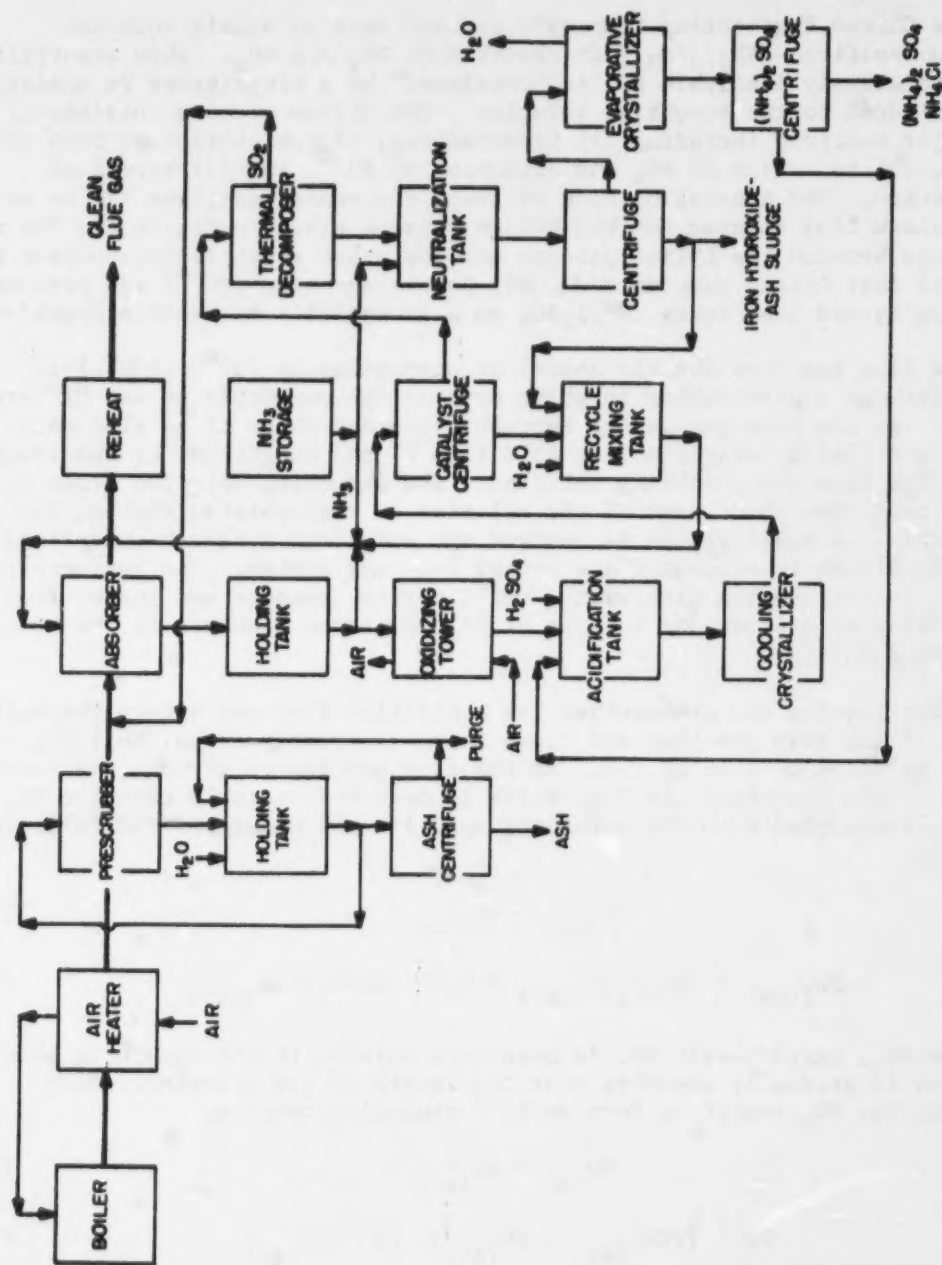
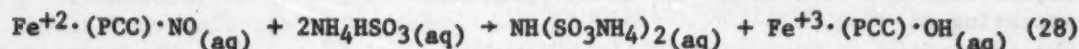
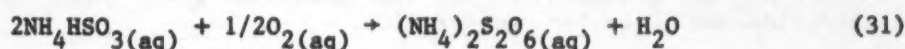
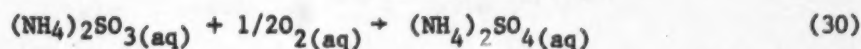


Figure 8. Flow Diagram of Chisso Engineering Process.

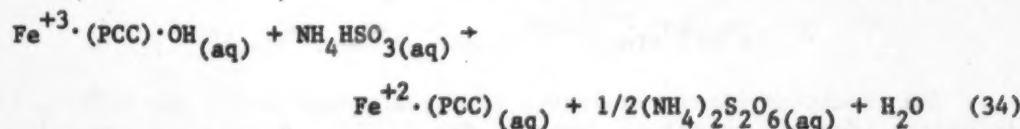
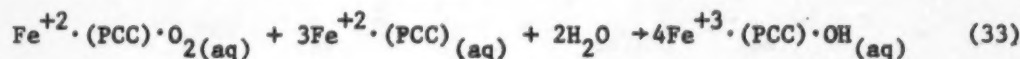
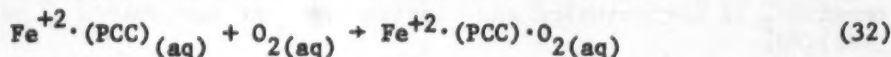
This Fe^{+2} chelate-NO complex reacts with the ammonium bisulfite $[(\text{NH}_4)\text{HSO}_3]$ to form either imidodisulfate $[\text{NH}(\text{SO}_3\text{NH}_4)_2]$ or amidosulfate $(\text{NH}_2\text{SO}_3\text{NH}_4)$. For example, the reaction for the formation of $\text{NH}(\text{SO}_3\text{NH}_4)_2$ is:



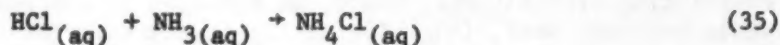
In addition to these primary reactions, other secondary reactions are occurring in the absorber including the oxidation of both the SO_3^- ion and the Fe^{+2} chelating compound by flue gas O_2 absorbed into the scrubbing solution. The reactions for the oxidation of the SO_3^- ion include:



The reactions involved in the oxidation and regeneration of the Fe^{+2} chelating compound are hypothesized to be the following:



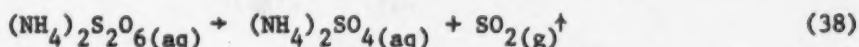
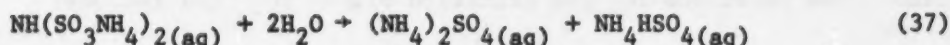
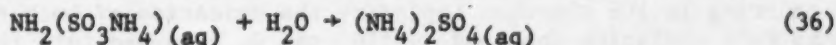
One other secondary reaction occurring in the absorber is that any remaining HCl in the flue gas will react with the scrubbing solution to form ammonium chloride (NH_4Cl) , i.e.,



The clean flue gas from the top of the absorber, after passing through a mist eliminator, is reheated and discharged through the stack.

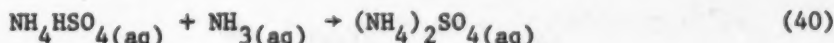
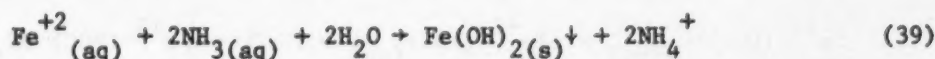
The scrubbing solution from the absorber drops to a holding tank from which most of the solution is recirculated through the absorber after makeup NH_3 has been added. The remainder of the scrubbing solution enters the regeneration section where the scrubbing solution is first pumped to an oxidizing tower. Inside this tower either air or O_2 is passed counter-currently to the NH_4^+ salt solution to convert the remaining SO_3^- and HSO_3^- salts to SO_4^- and S_2O_6^- by reactions (30) and (31).

The liquid effluent from the oxidizing tower is pumped to a catalyst recovery section, acidified with makeup H_2SO_4 , and sent to a cooling crystallizer to allow the catalyst to crystallize. The resulting slurry is pumped to a centrifuge to recover the solid catalyst for recycle while the mother liquor from the centrifuge is further processed in a thermal decomposer operating at about $120\text{--}140^\circ\text{C}$ ($248\text{--}284^\circ\text{F}$). Under these reaction conditions the $(\text{NH}_4)_2\text{S}_2\text{O}_6$ is decomposed while $\text{NH}(\text{SO}_3\text{NH}_4)_2$ and $\text{NH}_2(\text{SO}_3\text{NH}_4)$ are hydrolyzed into $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 by the following reactions.



The SO_2 gas generated in the decomposition of the $(\text{NH}_4)_2\text{S}_2\text{O}_6$ is recycled to the flue gas ducts for reabsorption.

The hot liquid effluent from the decomposer is pumped to a neutralization reactor where NH_3 is injected. This conversion from an acidic to a basic solution results in the precipitation of iron hydroxide $[\text{Fe}(\text{OH})_2]$ from the remainder of the solution and, indirectly, the conversion of NH_4HSO_4 to $(\text{NH}_4)_2\text{SO}_4$.



The resulting slurry is pumped to a centrifuge where the $\text{Fe}(\text{OH})_2$ is recovered from the solution. Most of the $\text{Fe}(\text{OH})_2$, along with the solid catalyst separated earlier, is redissolved and recycled to the absorber. A small portion of the $\text{Fe}(\text{OH})_2$, however, is removed from the system as a waste sludge to prevent the buildup of the ash in the circulating solution. The liquid from the centrifuge, containing mainly $(\text{NH}_4)_2\text{SO}_4$, is sent to an evaporating crystallizer, where the solution is concentrated, using indirect steam heating, until $(\text{NH}_4)_2\text{SO}_4$ begins to crystallize. After cooling to allow crystal growth, the resulting crystals are removed in a centrifuge and conveyed to a byproduct storage section. The mother liquor, containing mainly $(\text{NH}_4)_2\text{SO}_4$, is recycled to the acidification reactor.

Status of Development

The Chisso NH_3 scrubbing process has only been tested on a bench-scale unit of $300 \text{ Nm}^3/\text{hr}$ (0.1 MW equiv) at the Chisso Petrochemical Company's Goi plant. However, the entire process including both the absorption and regeneration sections was tested as a single unit. The flue gas was from an oil-fired boiler and contained 1600 ppm SO_2 , 200 ppm NO_x , 4% O_2 , and a dust level of $0.05\text{--}0.1 \text{ g/Nm}^3$ [$0.0215\text{--}0.0430 \text{ g/ft}^3$ (32°F)]. The longest continuous operation of this bench-scale unit was said to be about 2 wk (335 hr) and reportedly achieved 95% SO_2 removal and 80% NO_x removal.

Although this wet simultaneous process has not been tested on coal-fired flue gas, Chisso believes that with the removal of some of the precipitated $\text{Fe}(\text{OH})_2$ -ash sludge from the system, the ash levels in the circulating solution can be controlled at a moderate level and thus this process could handle the increased particulate loading associated with coal combustion.

Since this process has only been tested on a laboratory scale, the next major development step should be a pilot-plant unit in the 1-10 MW range. Ideally this pilot plant would be able to test the applicability of this process for treating flue gas from a coal-fired boiler, as well as flue gas from an oil-fired boiler.

Background of Process Developer

Chisso Engineering Company is a subsidiary of Chisso Corporation, which is a major fertilizer producer in Japan. Prior to the development of this process, which is based on the original NH_3 scrubbing system of Catalytic, Inc., Chisso apparently had very little previous experience in FGT of either SO_2 or NO_x . The development of this process was begun in 1973 with the laboratory testing of both SO_2 and NO_x removal efficiencies using an $(\text{NH}_4)_2\text{SO}_3$ scrubbing solution containing their special catalyst. The following year bench-scale tests were completed to test the regeneration system and also the effects of other flue gas species, particularly O_2 , on the absorption efficiencies. In 1975 bench-scale testing was begun at the Chisso Goi installation using the entire system as a single unit.

Chisso has recently licensed Catalytic to market, engineer, and construct plants utilizing this process in the U.S.

Published Economic Data

Since this process has only been tested on a bench-scale unit, the following published economic data should be considered as a preliminary estimate and subject to revision. Chisso estimates (97) the total capital investment for a system to treat $150,000 \text{ Nm}^3/\text{hr}$ of flue gas from a heavy oil-fired boiler containing 1,600 ppm SO_2 and 200 ppm NO_x as 1,464 million yen (assumed construction basis: Japan and 1976 costs). If 300 yen/\$ and $3,000 \text{ Nm}^3/\text{hr}/\text{MW}$ are assumed, this corresponds to a total capital investment of \$4,880,000 for a 50-MW system or approximately \$98/kW of installed capacity. The estimated revenue requirements for this wet simultaneous SO_2 - NO_x system were estimated as 7915 yen/kl of oil (95% desulfurization and 80% denitrification). Using the same assumptions listed above this corresponds to a revenue requirement of about 6.6 mills/kWh for simultaneous SO_2 and NO_x removal.

Raw Materials, Energy, and Operation Requirements

The following raw material requirements are estimated by Chisso based on a plant treating $150,000 \text{ Nm}^3/\text{hr}$ (50 MW equiv) of flue gas. This flue gas from an oil-fired boiler was assumed to contain 1600 ppm SO_2 , 200 ppm NO_x , 4% O_2 , and 0.05-0.1 g/ Nm^3 of particulates. SO_2 and NO_x removal efficiencies were assumed to be 95% and 80% respectively.

<u>Material</u>	<u>Quantity required</u>
Liquid NH_3	425 kg/hr
H_2SO_4 (98%)	340 kg/hr
Catalyst makeup	\$25/hr

The utility requirements using the same basis were estimated as:

<u>Utilities</u>	<u>Quantity required</u>
Steam	6,000 kg/hr
Cooling water	700 m^3 /hr
Process water	10 m^3 /hr
Electric power	1,800 kW

This electrical requirement represents 3.6% of the total generating capacity of the boiler.

The byproducts produced include solid $(\text{NH}_4)_2\text{SO}_4$ containing some NH_4Cl and a small amount of $\text{Fe}(\text{OH})_2$ -flyash sludge. For the assumptions listed above, approximately 1700 kg/hr of $(\text{NH}_4)_2\text{SO}_4$ would be produced.

The estimated operating manpower, including maintenance personnel for this system, would be two men per shift plus two men per day.

Technical Considerations

The Chisso process, although very similar to other wet, absorption reduction processes, particularly in the absorption section, is less complex overall. However, many pieces of process equipment are required in the regeneration section including: three centrifuges, two crystallizers, one thermal decomposer, one oxidizing tower, and five assorted tanks or reactors. In addition there will be at least four large tray absorbers for each 500-MW plant. On the other hand there are relatively few requirements for solids-handling equipment and also the temperatures in the regeneration section are less severe than those in some of the other absorption-reduction processes. Thus the overall process control requirements, although much more complex than the dry SCR processes, will probably be similar in complexity to the other wet, absorption-reduction processes.

The process developers suggest that, since this is a wet process, the increased particulate and Cl^- loadings associated with coal combustion will not present significant problems in adapting their process to treat flue gas from a coal-fired boiler. The only modifications envisioned by Chisso to prevent the buildup of these particulates in the circulating solution is the addition of a prescrubber and associated process equipment to remove most of the ash before the flue gas reaches the absorber and also a small purge stream to remove some of the ash-contaminated $\text{Fe}(\text{OH})_2$ sludge from the circulating solution. The Cl^- will be removed primarily in the prescrubber with a minor amount purged as an NH_4Cl contaminant in the $(\text{NH}_4)_2\text{SO}_4$ byproduct stream.

The Chisso NH_3 scrubbing process has been tested on a bench-scale unit treating flue gas containing 1600 ppm SO_2 , 200 ppm NO_x , 4% O_2 , and 0.05-0.1 g/ Nm^3 of dust. During a 2-wk continuous test, this process was able to maintain 95% SO_2 and 80% NO_x removal efficiency. The removal efficiency for SO_2 is relatively insensitive to both the operating condition in the absorber and the inlet gas conditions because the L/G ratio required in the absorber to remove the relatively insoluble NO is much higher than that required for FGD only. The NO_x removal efficiency, however, is dependent on both the SO_2 and the O_2 content of the flue gas. The reasons for this dependency are the same as were given for the other absorption-reduction processes, that is, the SO_2 , once absorbed into solution as the $\text{SO}_3^{=}$ ion, is used to reduce the absorbed NO_x . When either the O_2 content in the flue gas is high or the SO_2 concentration in the flue gas is low, less of the $\text{SO}_3^{=}$ ion is available to reduce the NO_x . For a flue gas stream containing 2400 ppm SO_2 , 600 ppm NO_x , and 4.5% O_2 , only about 80% NO_x removal can be expected.

Since the overall absorption section for the Chisso process is very similar to that for the other absorption-reduction processes, many of the parameters and conclusions for the Chisso absorption system will probably be similar to those listed for the other absorption-reduction processes. The L/G ratio in the absorber will probably range from 10-15 l/ Nm^3 (65-100 gal/kaf t^3 at 127°F) depending on both the concentration of the NO_x in the flue gas and the removal efficiency required. For flue gas containing 600 ppm NO_x and L/G ratio in the upper portion of this range, probably approaching 15 l/ Nm^3 (100 gal/kaf t^3 at 127°F), would be required. In addition the superficial gas velocity through the absorber will probably be in the range of 1-2 m/sec (3-7 ft/sec). These two parameters indicate that the absorbers for the Chisso process will be much larger than conventional limestone desulfurization scrubbers.

The large difference in the solubilities of SO_2 and NO leads to the unique situation in the absorber where the SO_2 is rapidly stripped from the flue gas in the lower portion of the absorber while the NO is more gradually removed throughout the absorber. This occurrence is one of the primary reasons why the Fe^{+2} chelating compound is a major constituent of the scrubbing solution. Since the Fe^{+2} chelating compound forms a complex with the absorbed NO, it not only stimulates further NO absorption by the scrubbing solution, but also binds the NO and transports it to the lower portion of the absorber where a higher concentration of absorbed SO_2 , i.e., the $\text{SO}_3^{=}$ ion, is available to reduce the NO.

Another major reason for the high concentration of Fe^{+2} chelating compound in the scrubbing solution is that a substantial portion of the Fe^{+2} ion is oxidized during passage through the absorber by O_2 absorbed from the flue gas and is not available to absorb NO. (The NO apparently combines with the Fe^{+2} ion in a complex form which the Fe^{+3} ion is not capable of forming.) Thus, a relatively high concentration of the Fe^{+2} chelating compound is required to furnish enough reaction sites for acceptable NO removal.

Since this is a wet removal system the major consideration in retrofitting this system to existing coal-fired boilers will be the land necessary for the process equipment and for a landfill area for both the flyash and a minor amount of $\text{Fe}(\text{OH})_2$ -ash sludge.

The process should have relatively good turndown capabilities since the absorption system contains four scrubber trains, any combination of which could be shut down completely. However, during turndown the NO_x removal efficiency will decline at least somewhat since in general when the boiler load is reduced the airflow is not correspondingly decreased. Thus, the flue gas will contain a higher concentration of O_2 and a lower concentration of SO_2 .

The incoming flue gas ducts should be constructed of Inconel 625 to prevent corrosion while most of the remaining process equipment and piping should be elastomer-lined carbon steel to prevent corrosion problems associated with circulating Cl^- solutions. The only major piece of equipment not elastomer lined should be the decomposer which will be constructed of glass-lined steel.

Environmental Considerations

The Chisso process, during a test on oil-fired flue gas (1600 ppm SO_2 , 200 ppm NO_x , and 4% O_2) in a laboratory bench-scale unit (0.1 MW equiv), was able to achieve 95% SO_2 removal and 80% NO_x removal. The absorbed NO_x is reduced to NH_3 while the SO_2 is absorbed as SO_3^- and oxidized to SO_4^- . Then, by simply combining the NH_3 and the SO_4^- , byproduct $(\text{NH}_4)_2\text{SO}_4$ is formed. As was stated earlier, the SO_2 removal is insensitive to changes in the inlet gas composition or the absorber operating conditions. The NO_x removal efficiency is, however, sensitive to both the O_2 and the SO_2 content of the flue gas. This could present a problem for flue gas from a boiler fired with low-S coal.

Critical Data Gaps and Poorly Understood Phenomena

The major critical data gaps for the Chisso process include the following:

1. L/G ratio in the absorber
2. Scrubbing solution composition
3. Operating conditions and stream flows in the process equipment in the regeneration section
4. Marketability of byproduct $(\text{NH}_4)_2\text{SO}_4$ in the U.S.
5. Method of preventing sulfitic plume from the stack

The poorly understood phenomena would include the actual series of reactions involved in the absorption and reduction sections. Although hypothesized reactions are given by Chisso for the absorption and reduction of NO_x , others have given different reactions for these steps. Also, their method to eliminate the formation of sulfitic plume is not specified and in previous studies (106) this has been a significant problem.

Advantages and Disadvantages

The Chisso NH_3 scrubbing process has the following advantages and disadvantages over other wet processes as well as the dry NO_x processes.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Produces a potentially marketable byproduct $\text{[(NH}_4\text{)}_2\text{SO}_4\text{]}$
4. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

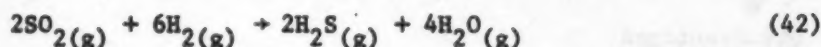
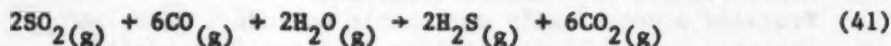
1. Requires significant amounts of energy for the regeneration step
2. Has not been tested on coal-fired flue gas
3. Has been tested only in a bench-scale unit
4. Has not been operated for a long-term continuous period
5. Incorporates design features which may present significant process control problems
6. Uses significant amounts of stainless steel or exotic materials for process equipment
7. Has a low superficial gas velocity in the absorber (<10 ft/sec)
8. Has a high L/G ratio in the absorber (>70 gal/kaft³)
9. Requires flue gas reheat for plume buoyancy
10. Requires flue gas constituents within specific ranges for high NO_x removal
11. Requires an expensive liquid-phase catalyst

Process Modifications Suggested by Cooperating Companies to Overcome Some Technical Disadvantages (94)

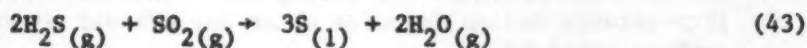
To overcome two of the main drawbacks of the basic Chisso NH_3 -scrubbing process--the sulfitic plume from the absorber and the formation of a relatively unmarketable byproduct $\text{[(NH}_4\text{)}_2\text{SO}_4\text{]}$ --Catalytic has modified the original absorber and also added the Institut Francais du Petrole (IFP) S recovery process to the original Chisso scheme.

By redesigning the original tray-type absorber and converting it to a multistage unit with individual liquid recirculation for each stage, the operating conditions are expected by Catalytic to be carefully controlled such that the characteristic sulfitic plume is eliminated. As the flue gas is passed through each successive stage of the tower, the concentration of NH_3 in the scrubbing solution is gradually decreased from stage to stage. As a final treatment step, the final stage in the absorber contains a weak circulating acid solution to remove most of the remaining NH_3 and thus minimize the NH_3 emissions from the system. This use of progressively decreasing NH_3 concentrations in the scrubbing solutions from the first to the last stage in the absorber, coupled with the decreasing SO_2 concentration in the flue gas and the acid scrubbing in the final stage, is said to eliminate the sulfitic plume normally associated with NH_3 -scrubbing processes such as the original Chisso system.

The second major modification of the original Chisso system is the elimination of the byproduct $(\text{NH}_4)_2\text{SO}_4$ recovery section. As an alternate scheme, the $\text{SO}_4^{=}$ solution from the $\text{Fe}(\text{OH})_2$ centrifuge is pumped to an IFP recovery section (see flow diagram in Figure 9). The NH_4^+ -salt solution is first pumped to an evaporator to remove the excess H_2O and then the remaining $\text{SO}_4^{=}$ is combined with molten S and sent to an $\text{SO}_4^{=}$ reducer operating at 370°C (700°F) where the $\text{SO}_4^{=}$ is converted to NH_3 , H_2O , and SO_2 . These gaseous products are reacted with a reducing gas over a proprietary catalyst to form hydrogen sulfide (H_2S), i.e.,



The resulting product stream is cooled to 160°C (320°F) and enters a liquid Claus unit where molten S produced by the following reaction is removed as byproduct.



The off-gases of the Claus unit, primarily H_2O and NH_3 , enter an aqueous stripper where the NH_3 is removed prior to exhausting the waste gas. The aqueous NH_3 solution recovered in the stripper is concentrated by steam distillation and recycled to the NH_3 solution storage tank.

This IFP system has been tested on a 30-MW prototype unit at a power plant near Paris, France, while the absorber has been tested at Catalytic's 2-MW-equiv engineering optimization unit operating on a coal-fired boiler at Calvert City, Kentucky.

The increased capital investment and revenue requirements associated with the absorber have not been released but the costs for the IFP process for a 500-MW coal-fired boiler (3.5% S coal, 90% SO_2 removal, 7000 hr/yr) have been estimated (15) as approximately \$40/kW of generating capacity and 2.0 mills/kWh respectively.

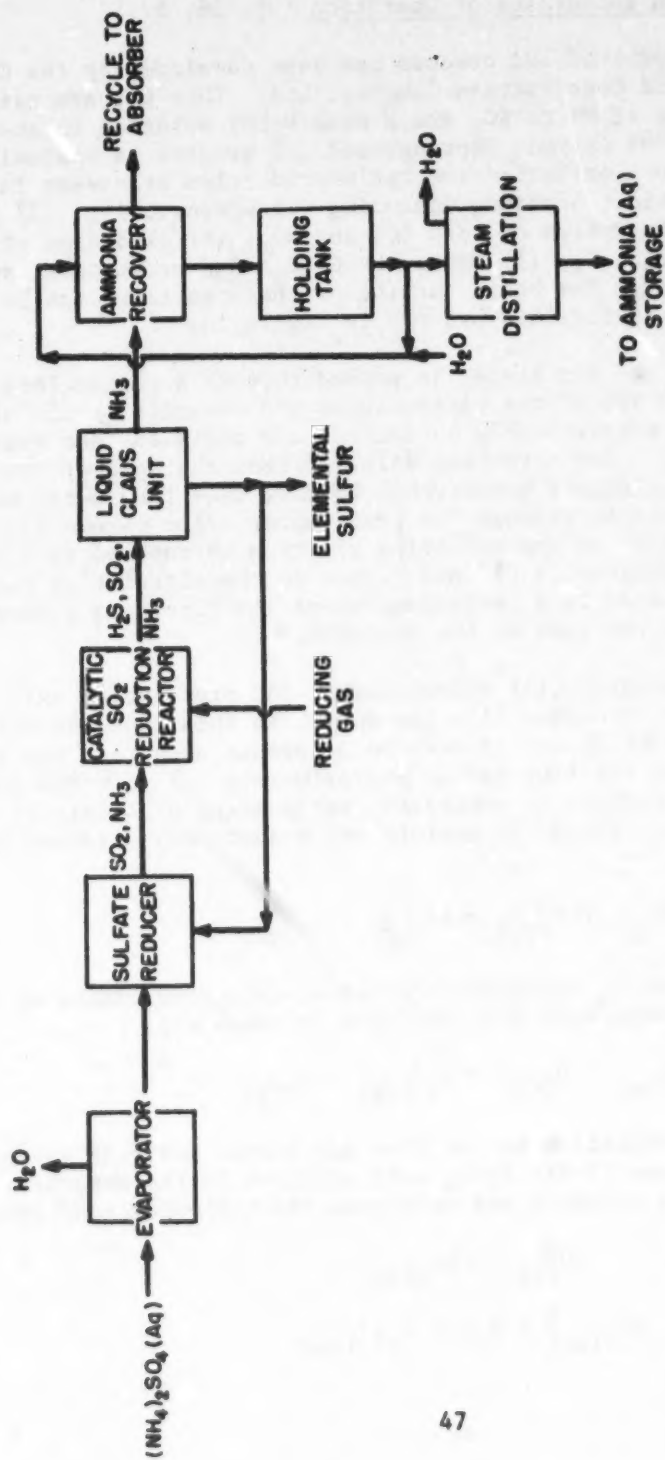


Figure 9. Flow Diagram of IFP S Recovery Process.

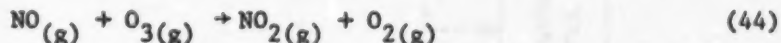
CHIYODA THOROUGHbred 102 PROCESS - WET, OXIDATION-ABSORPTION-REDUCTION ($\text{NO}_x\text{-SO}_x$)

Process Description and Principles of Operation (35, 36, 57)

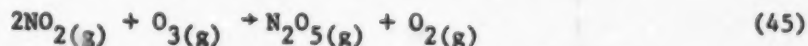
The Chiyoda Thoroughbred 102 process has been developed by the Chiyoda Chemical Engineering and Construction Company, Ltd. This process uses O_3 for the gas-phase oxidation of NO to NO_2 and a weak H_2SO_4 solution to absorb both the SO_2 and the NO_2 . The Chiyoda Thoroughbred 102 process is basically similar to the other wet, oxidation-absorption-reduction processes in that it consists of six distinct sections including (1) prescrubbing, (2) gas-phase oxidation of NO , (3) absorption of both SO_2 and NO_x , (4) oxidation of SO_3 and reduction of absorbed NO_x , (5) byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production, and (6) wastewater treatment. The basic outline of these sections can be seen in the block flow diagram for this process in Figure 10.

The flue gas from the air heater is passed through a particulate prescrubber, which removes 90% of the particulates and essentially all of the HCl from the gas, also adiabatically humidifies and cools the gas from 150°C (300°F) to 53°C (127°F). The scrubbing solution from the base of the prescrubber drops to a particulate prescrubber holding tank from which most of the solution is recirculated through the prescrubber after makeup H_2O has been added. The remainder of the scrubbing solution is removed as a purge stream to prevent the buildup of Cl^- and flyash in the circulating solution. This purge stream is pumped to a centrifuge where the flyash is removed and the centrate is sent to the base of the absorber.

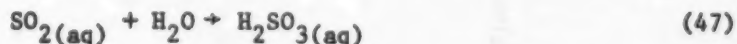
The gas passes through a mist eliminator at the prescrubber exit and is sent to the absorber through a flue gas duct. In this duct the gas is injected with a weak (<5%) O_3 -air mixture in an amount such that the resulting mol ratio of O_3 to NO in the flue gas is approximately 1.5 (for 80% NO_x removal). This O_3 -air mixture is generated onsite using a battery of corona-discharge O_3 generators. The NO is rapidly and selectively oxidized by the O_3 to NO_2 .



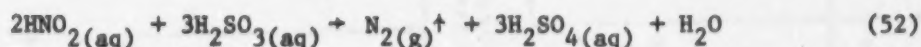
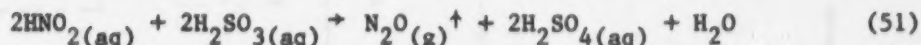
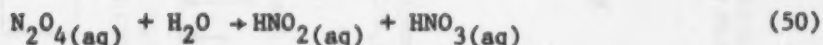
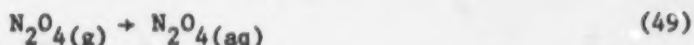
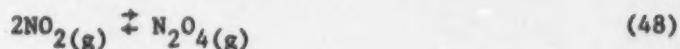
By positioning these O_3 injection nozzles to give good mixing of the gases, the following undesirable side reaction is minimized.



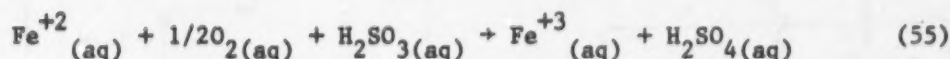
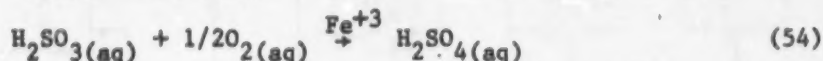
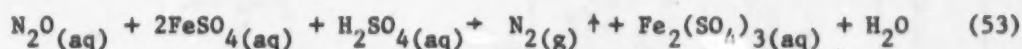
Following this O_3 oxidation in the flue gas ducts, the flue gas passes countercurrently to a weak (2-3%) H_2SO_4 acid solution in the absorber. The SO_2 is absorbed into the solution and undergoes the following reactions.



NO_x on the other hand is absorbed into the solution as the dimer molecule (N₂O₄) and undergoes the following reactions.

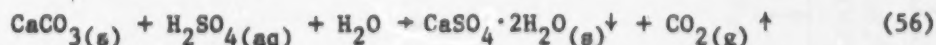


In addition to these primary reactions occurring in the absorption section of the vessel, other secondary reactions occur simultaneously.



The scrubbed flue gas is passed through a mist eliminator, reheated for plume buoyancy, and sent to the stack.

The liquid effluent from the absorber is pumped to an oxidation tower where any remaining dissolved SO₂ is converted to H₂SO₄. The oxidation catalyst (Fe⁺³) is also regenerated during its passage through the oxidation tower (reaction 55). Most of the liquid solution is recycled to the absorber while a small bleed stream is removed and is initially sent to a holding tank in the byproduct recovery section. From this holding tank the weak H₂SO₄ solution is pumped to a unique reaction crystallizer patented (44) by Chiyoda (see Figure 11). This solution is pumped into the middle section of the crystallizer and pushed up by an air stream injected below the H₂SO₄ solution. Near the top of the crystallizer makeup limestone is added to the H₂SO₄ and the following reaction occurs.



The CaSO₄·2H₂O crystals formed by this reaction are suspended in the upward flowing air-solution mixture and overflow into the outer portion of the annular crystallizer. Air is also injected into the outer region of the crystallizer to suspend the large number of small CaSO₄·2H₂O crystals in the mother liquor and allow these crystals to coalesce and grow into larger crystals. These crystals will remain suspended in the crystallizer until they have reached the predetermined size and overcome the force of the air passing through the solution. After these crystals have separated and

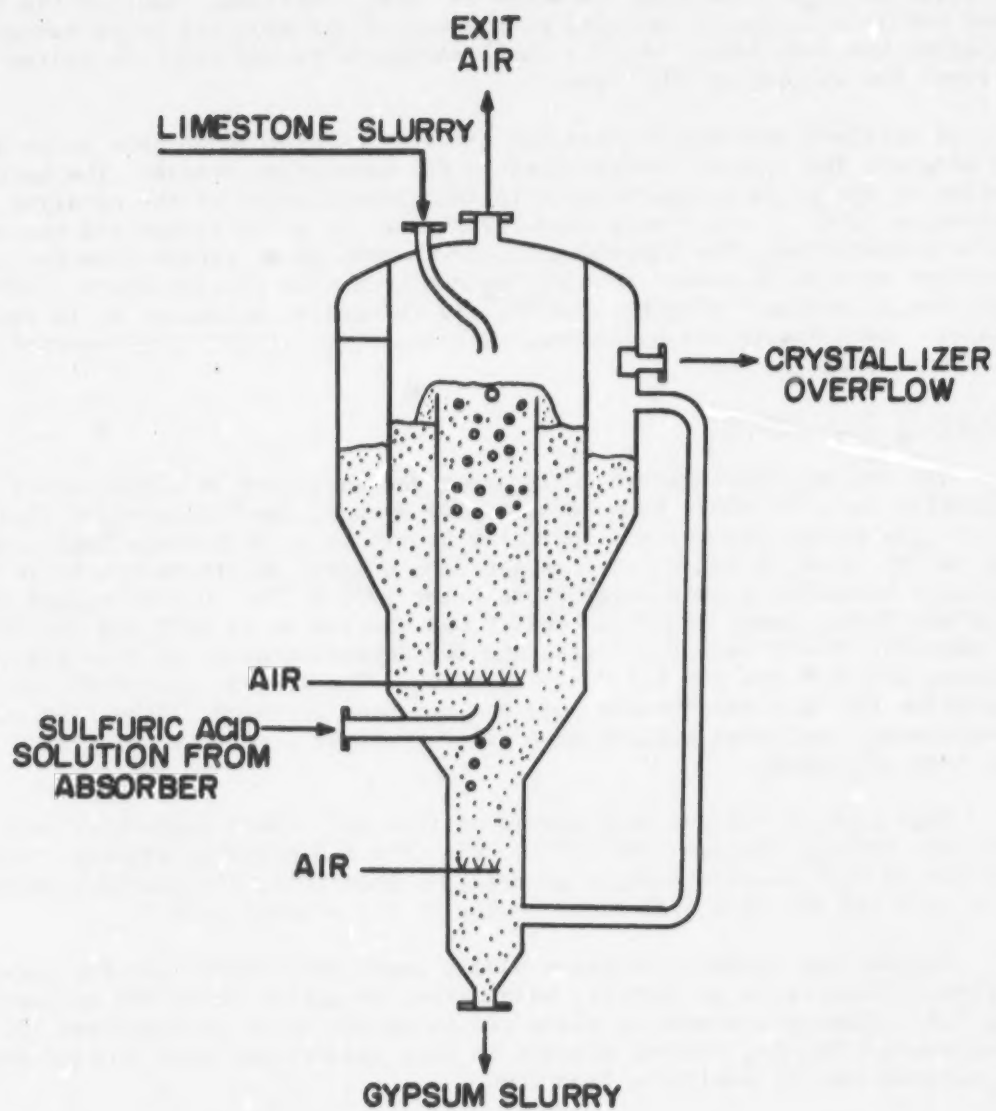


Figure 11. Chiyoda Reaction Crystallizer (44).

settled to the bottom of the crystallizer, they are removed in a bottoms slurry and pumped to a centrifuge where the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is separated and sent to a byproduct storage area. The mother liquor from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ centrifuge and the overflow from the reaction crystallizer are pumped to a thickener where the bottoms containing mainly undersized $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals, are recycled to the crystallizer to serve as "seed" crystals. Most of the thickener overflow stream is recycled to the top of the absorber after makeup catalyst has been added, while a small amount is purged from the system to prevent the buildup of NO_3^- ions.

A catalyst recovery section has recently been added to this purge stream to minimize the loss of the catalyst in the wastewater stream. The neutralization of the purge stream results in the precipitation of the catalyst as a hydroxide $[(\text{OH})^-]$ and thus allows its removal in a centrifuge and its recycle to be redissolved. The remaining liquid in this purge stream from the catalyst recovery section is pumped to a biological treatment section where, with the addition of methanol (CH_3OH), the NO_3^- is reduced to molecular N_2 in two stages. Both stages are biological with the first stage being anaerobic and the final stage aerobic.

Status of Development

The Chiyoda Thoroughbred 102 process was developed by adding an O_3 injection stage to their more advanced FGD system, the Thoroughbred 101 process. The former process was initially tested in a bench-scale unit treating $200 \text{ Nm}^3/\text{hr}$ (0.06 MW equiv) of flue gas from a heavy oil-fired boiler in 1973. A larger bench-scale unit designed to treat $1000 \text{ Nm}^3/\text{hr}$ (0.3 MW equiv) of flue gas from a heavy oil-fired boiler was started up in 1975 and was able to maintain 90-98% desulfurization and 80% denitrification on flue gas containing 500-2000 ppm SO_2 and 80-250 ppm NO_x . The longest period of continuous operation for this bench-scale unit has not been revealed. Plans for further development, including scaleup to a pilot plant or prototype unit, also have not been published.

This process has not been tested on flue gas from a coal-fired unit although Chiyoda Thoroughbred 101 process (the FGD system), which is very similar to this denitrification process, is undergoing testing in a prototype unit (20 MW) on a coal-fired boiler at the present time.

Chiyoda has recently formed a wholly owned subsidiary, Chiyoda International Corporation in Seattle, Washington, to market their FGD system in the U.S. Chiyoda has made no plans yet to market their Thoroughbred 102 simultaneous SO_2 - NO_x removal process in this country and only limited amounts of information are available from them.

Background of Process Developer

Chiyoda is a well-known Japanese company with design and construction projects around the world. They have been involved in air pollution control since the early 1970's, first in the development of an FGD process and later modifying this process to simultaneously remove both SO_2 and NO_x . The 13 prototype and commercial FGD plants built by Chiyoda for treating flue gas

from heavy oil-fired boilers range in size from 20-350 MW. During 1975 a 23-MW prototype plant was started up and operated to test the ability of the Chiyoda FGD process to treat flue gas from a coal-fired boiler at the Scholz Steam Plant of Gulf Power.

Chiyoda's desulfurization process (Thoroughbred 101) was converted to simultaneously remove $\text{SO}_2\text{-NO}_x$ in 1975 by simply adding an O_3 injection system to the desulfurization pilot plant. This modified desulfurization process was renamed the Thoroughbred 102 process and tested first in a bench-scale plant (0.06 MW equiv) and later in 1975 in a large (0.3 MW equiv) bench-scale unit.

Published Economic Data

The following capital investment and revenue requirements for the Chiyoda Thoroughbred 102 processes are based on treating $750,000 \text{ Nm}^3/\text{hr}$ of oil-fired flue gas containing 1,000 ppm SO_2 and 150 ppm NO_x and on SO_2 and NO_x removal efficiencies of 90 and 80% respectively. Under these conditions the total capital investment has recently been estimated (36) as 8000×10^6 yen and the revenue requirement as 8400 yen/kl of oil (assumed basis: Japan and 1976 costs). If 300 yen/\$ and $3000 \text{ Nm}^3/\text{hr}/\text{MW}$ are assumed, this corresponds to a capital investment of \$107/kW of generating capacity and a revenue requirement of 6.73 mills/kWh. In addition to these total costs, Chiyoda has estimated the capital investment and revenue requirements for the O_3 generating system as \$40/kW and 2.72 mills/kWh respectively. Thus the cost of generating O_3 represents approximately 38% of both the capital investment and also the revenue requirements for this system.

Raw Materials, Energy, and Operation Requirements

The major raw material requirements for the Chiyoda Thoroughbred 102 process are limestone for the neutralization reaction to produce byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and O_3 for the conversion of NO to NO_2 . However, since the O_3 will be generated onsite with only the consumption of electricity and air, it will not be considered as a raw material requirement but as an energy requirement. The only other raw material needed for this process is the oxidation catalyst, ferric sulfate $[\text{Fe}_2(\text{SO}_4)_3]$, which is lost in the byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ stream. No data have been published on the quantities of the raw materials required for this process.

The major energy requirements for this process include fuel oil for reheating the flue gas and electricity, mainly for O_3 generation but also for operating the process equipment. The only other utility requirements would be for cooling H_2O and process air. No data are available on these utility requirements.

Technical Considerations

The Chiyoda Thoroughbred 102 process uses O_3 for the gas-phase oxidation of NO and a weak H_2SO_4 -scrubbing solution to absorb the resulting NO_2 . This system appears to require approximately the same number and type of process equipment as other oxidation-absorption-reduction processes and hence the

process control problems will be very similar to these other processes. Since O_3 cannot be stored but must be generated onsite, the major process control problem will be the control of the O_3 generation and injection system. If the O_3 is injected in less than stoichiometric amounts, the NO_x removal efficiency will decline and, if O_3 is injected in more than stoichiometric amounts, the annual revenue requirements for this system will increase sharply since the cost of generating O_3 is one of the major economic factors associated with this process.

NO_x removal efficiency is relatively insensitive to the inlet gas composition. In the case of the Thoroughbred 102 process, this insensitivity is due primarily to the fact that only approximately 50% of the absorbed NO_x is reduced by the SO_3^{2-} ion to molecular N_2 . The remainder of this absorbed NO_x leaves the system as NO_3^- salts without undergoing reduction by the SO_3^{2-} ion.

The absorber and oxidizer operating conditions have not been specified but the primary concern will probably be the costs associated with circulating these large volumes of solution between the absorber and the oxidizer. Chiyoda has recently designed a combined absorber-oxidizer for their Thoroughbred 101 FGD process and its adaption for use in the Thoroughbred 102 simultaneous SO_2 - NO_x process would substantially reduce these costs.

Although the Thoroughbred 102 process has not been tested on flue gas from a coal-fired boiler, Chiyoda does not expect any serious technical problems in modifying this system to handle the increased particulates and Cl^- associated with coal combustion. The major reason for this confidence is their previous experience in modifying their Thoroughbred 101 FGD system to handle coal-fired flue gas at a 23-MW prototype unit which has been operating at the Scholz Steam Plant for the past year. The only major modification was the separation of the prescrubber section from the absorber section, that is, the prescrubber at the Scholz plant is a closed-loop operation with ash and Cl^- removed from the prescrubbing solution and the "cleaned" solution recycled back to the prescrubber instead of being pumped to the absorber as was previously done in oil-fired flue gas applications.

The adaptation of this process to treat coal-fired flue gas will, however, create some economic problems. The increase in inlet NO_x concentration in the flue gas in converting from oil to coal will cause a proportionate increase in the amount of O_3 required and thus substantially increase the annual revenue requirements for this process.

The $CaSO_4 \cdot 2H_2O$ produced as a byproduct will contain numerous salt impurities including calcium nitrate $[Ca(NO_3)_2]$ and $Fe_2(SO_4)_3$. These salt impurities will however be present in lesser amounts in the $CaSO_4 \cdot 2H_2O$ cake from the Chiyoda process than in the $CaSO_4 \cdot 2H_2O$ from the other processes since Chiyoda has developed a unique reaction crystallizer which yields a $CaSO_4 \cdot 2H_2O$ product containing large crystals that are much easier to wash and centrifuge. For this reason the $CaSO_4 \cdot 2H_2O$ produced in this process, without further processing, is much more likely to find a market in the U.S. than the $CaSO_4 \cdot 2H_2O$ produced by the other processes.

It should be pointed out that the $\text{Fe}_2(\text{SO}_4)_3$ is present in the scrubbing solution to catalyze the oxidation of the SO_3^- ion in the scrubbing solution during its passage through the oxidizer and is not used to aid in the absorption of NO_2 .

The reasons behind Chiyoda's decision not to actively market this process have not been published but is probably a combination of the following reasons. The process is still in the early pilot-plant development stage. Secondly, the NO_3^- wastewater problem will be very difficult to treat in a large-scale unit and finally, the relatively low denitrification efficiency of the Chiyoda process as compared with the other NO_x removal systems. The reasons behind the apparent maximum NO_x removal rate of only 80% are not clear at the present time, but they are probably related to the selection of an H_2SO_4 solution to scrub the flue gas.

The purge stream from the regeneration section containing the NO_3^- will be treated in a two-stage biological treatment scheme. An excess of CH_3OH is added to the first stage under anaerobic conditions and the effluent from this reactor is pumped to the second stage where, under aerobic conditions, the excess CH_3OH is removed. The NO_3^- is converted to molecular N_2 which is then exhausted. The remainder of the purge stream is pumped to a disposal pond.

Since this is a wet simultaneous process, retrofitting this system on existing power plants should be relatively easy if sufficient land is available for the siting of the process equipment and holding ponds. The major modification would be removing the existing "cold" electrostatic precipitators (ESP) and installing a common plenum to connect the boilers to the four scrubber trains. The use of this common plenum and four scrubber trains will allow this system to be easily turned down by simply closing off any combination of scrubber trains. The ozone generation system can also be easily turned down since it is made up of a battery of smaller ozone generators.

The process equipment and piping for this system will be primarily made up of either stainless steel or elastomer-lined carbon steel depending on whether the equipment is in the absorption or regeneration section. The absorber section containing the circulating weak H_2SO_4 solution will require 316 stainless steel while those pieces of equipment in contact with the circulating $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ slurry will require elastomer-lined carbon steel. The incoming flue gas ducts, of course, will be constructed of Inconel 625 to prevent the corrosion associated with treating high-temperature, S-containing flue gas.

Environmental Considerations

During the operation of a pilot plant treating $1000 \text{ Nm}^3/\text{hr}$ (0.3 MW equiv) of flue gas from an oil-fired boiler (normal composition: 1500 ppm SO_2 , 150 ppm NO_x , 4% O_2), the SO_2 removal efficiency was typically 90-98% while the NO_x removal efficiency was approximately 80%. The SO_2 is absorbed as SO_3^- , oxidized to SO_4^- , and recovered as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The NO_x is oxidized by O_3 , absorbed into the solution, and removed from the system as either molecular N_2 or NO_3^- in the wastewater purge stream.

The NO_x removal efficiency for the Chiyoda process is dependent on the amount of O_3 injected as shown in Figure 12. As can be seen from this figure, from an economic point of view the optimum NO_x removal rate for the Chiyoda process is approximately 60%. Since one mol of O_3 oxidizes 1 mol of NO to NO_2 , this 60% NO_x removal occurs at an O_3 to NO_x ratio of 0.5. Since the generation of O_3 is extremely expensive, economically it would seem pointless to approximately triple one of the major operating costs to increase the NO_x removal efficiency from 60 to 80%. For high NO_x removal requirements, i.e., greater than 80%, this process would not be recommended.

The O_3 used to oxidize the NO in the flue gas is a significant work hazard associated with this process. This gas is a very strong oxidant and can be dangerous if workers are exposed to even low concentrations. The circulating H_2SO_4 solution, although relatively weak, is also a hazard for workers coming into contact with it.

Critical Data Gaps and Poorly Understood Phenomena

Included under critical data gaps and the preliminary engineering assumptions used to overcome these data gaps are:

1. The raw material and energy requirements.
2. The portion of the absorbed NO_x converted to NO_3^- salts in the wastewater. Assumed to be 50%.
3. The operating conditions in the absorber and the oxidizer.
4. Oxidation of H_2SO_3 in absorber? In oxidizer?
5. The minimum ratio of SO_2 to NO_x in flue gas for 80% NO_x removal without requirement for makeup sulfurous acid (H_2SO_3)?
6. Maintenance and manpower requirements.

Advantages and Disadvantages

The major advantages and disadvantages of the Chiyoda Thoroughbred 102 process are listed below.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Produces a potentially marketable byproduct ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
4. Is a slight modification of a commercially-available FGD system
5. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

1. Has not been tested on coal-fired flue gas
2. Has been tested only in a bench-scale unit
3. Uses significant amounts of stainless steel or exotic materials for process equipment
4. Requires flue gas reheat for plume buoyancy
5. Requires an expensive gas-phase oxidant
6. Incorporates unique treatment methods to prevent secondary sources of pollution (biological wastewater denitrification)

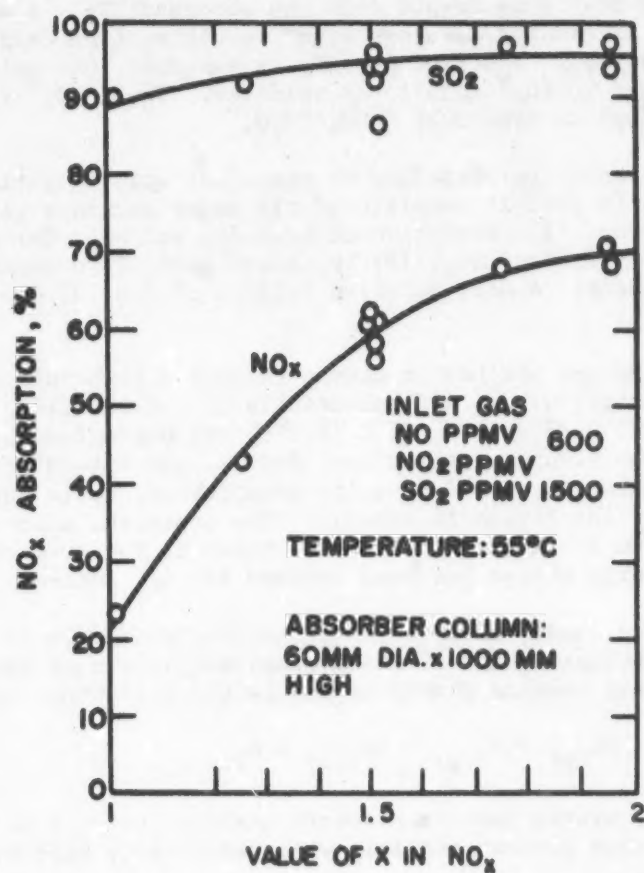


Figure 12. Effect of NO_x Oxidation Level on NO_x Absorption Efficiency for Chiyoda Process (113).

ISHIKAWAJIMA-HARIMA HEAVY INDUSTRIES PROCESS - WET, OXIDATION-ABSORPTION-REDUCTION (NO_x - SO_x)

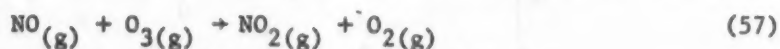
Process Description and Principles of Operation (11, 60, 116, 117)

In the Ishikawajima-Harima Heavy Industries (IHI) process the NO is oxidized to NO_2 by injecting O_3 into the flue gas stream. This NO_2 is then absorbed into the solution to form an equimolar aqueous mixture of NO_2^- and NO_3^- . Most of these NO_2^- and NO_3^- are reduced to molecular N_2 and complex N-S compounds by the SO_3^- ions formed from the absorbed SO_2 . A small amount of these NO_3^- salts is removed as a byproduct resulting from evaporation of a wastewater purge stream. The flue gas SO_2 is absorbed into solution as SO_3^- ions and oxidized to SO_4^- ions in an oxidizer. These SO_4^- ions are removed in a centrifuge as byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

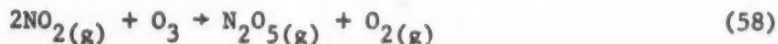
The overall system is very similar to the other wet, oxidation-absorption-reduction processes, in that it consists of six major sections (1) prescrubbing, (2) gas-phase oxidation, (3) absorption of both SO_2 and NO_x , (4) oxidation of SO_3^- and reduction of absorbed NO_x , (5) byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ recovery, and (6) wastewater treatment. A more detailed outline of the IHI process is shown in Figure 13.

The flue gas from the air heater passes through a prescrubber which removes most of the particulates and essentially all of the Cl^- . The flue gas is cooled from 150°C (300°F) to 53°C (127°F) and humidified by the evaporation of H_2O from the scrubbing solution. Most of the liquid effluent from the particulate scrubber is recycled to the prescrubber, while part is purged to a centrifuge where the flyash is removed. The centrate, although not specifically mentioned by IHI, is probably recycled to the prescrubber holding tank after a small purge stream has been removed for Cl^- control.

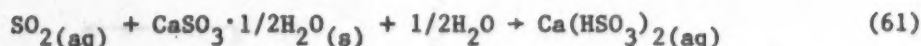
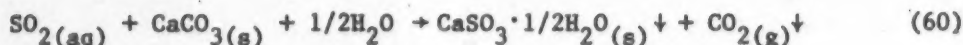
As the cooled gas passes through the connecting ducts, O_3 in a weak O_3 -air mixture, at approximately 80% of the stoichiometric amount required, is injected to selectively oxidize the NO to NO_2 by the following reaction:



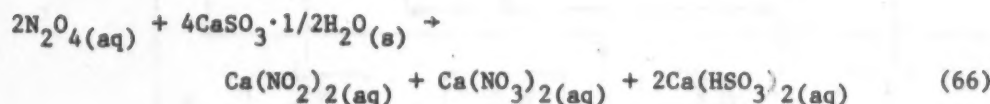
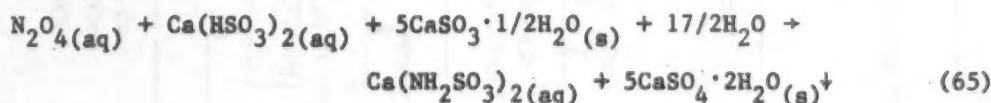
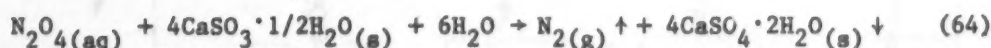
The O_3 injection system must be properly designed to give good mixing characteristics and thus prevent the following undesirable side reaction:



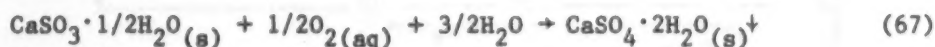
Following oxidation, the flue gas passes countercurrently to a lime or limestone slurry in a Turbulent Contact Absorber (TCA). This slurry at a pH of 4-6 also contains copper chloride (CuCl_2) and NaCl as catalysts at a concentration of about 0.005 molar to aid in the absorption of NO_2 . The SO_2 is absorbed from the flue gas and undergoes the following liquid-phase reactions:



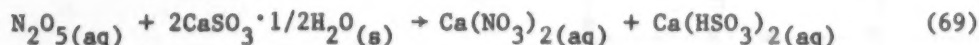
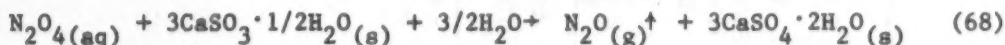
The NO_2 is absorbed and undergoes the following reactions in the scrubber solution.



In addition to these primary reactions, the other secondary reactions are occurring in the absorbing solution. O_2 is also absorbed from the flue gas and oxidizes this SO_3^- and SO_4^- by the following reaction.



The NO_x , including some N_2O_5 , can also undergo the following reactions.



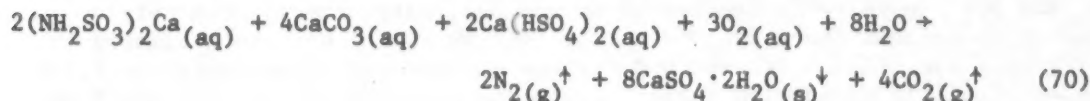
Thus the SO_2 , absorbed to form the SO_3^- ion, is used to reduce the NO_2 to molecular N_2 and to complex N-S compounds. Approximately 80% of the absorbed NO_x is converted to calcium sulfamates $[\text{Ca}(\text{NH}_2\text{SO}_3)_2]$ and most of the remainder to molecular N_2 . According to the process developer, byproduct NO_3^- - NO_2^- salts represent only a small amount (<10%) of the total absorbed NO_x .

After passing through a mist eliminator, this cleaned flue gas is reheated to provide plume buoyancy and is then exhausted through the stack.

From the absorber, the solution flows into a holding tank where small amounts of fresh catalyst (as required) and either slaked lime or limestone are added. Most of this slurry is recycled to the absorber while a small (1-2% of the circulating solution) stream is sent to an oxidizing tower in the regeneration section. Any $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ remaining in this purge stream is converted to CaSO_4 as it passes countercurrently to an air stream in the oxidizing tower. This CaSO_4 slurry from the oxidizing tower is then centrifuged to remove byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The final treatment step for the centrate, which contains the complex N-S compounds and the NO_3^- salts, has not been firmly established as yet. IHI offers three alternative methods for treating this system (1) evaporation and atmospheric thermal decomposition of the N-S compounds, (2) pressurized thermal decomposition, or (3) chemical decomposition method. Each of these treatment methods would form molecular N_2 but would be expensive.

At the present time IHI is apparently favoring the evaporation-decomposition method for removing the NO_3^- and $\text{Ca}(\text{NH}_2\text{SO}_3)_2$ from the wastewater stream. The liquor from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ centrifuge is first neutralized with limestone slurry to prevent the formation of NH_3 and pumped to a thickener. The bottoms stream from the thickener, containing mostly excess limestone slurry, is removed and recycled to the absorber. The thickener overflow is pumped to a steam evaporator to concentrate the solution before entering the thermal decomposer. At the higher temperatures in the decomposer the $\text{Ca}(\text{NH}_2\text{SO}_3)_2$ and the NO_3^- salts are decomposed to molecular N_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The decomposition of the $\text{Ca}(\text{NH}_2\text{SO}_3)_2$ is given by the following reaction.



The off-gas may contain some SO_2 in addition to the N_2 and CO_2 and will be recycled to the flue gas ducts. The remaining slurry from the decomposer containing mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will be centrifuged and the centrate will be purged.

Status of Development

The initial development work for the IHI process was done on a bench-scale unit treating simulated flue gas. Bench-scale testing was begun in mid-1974 in a 500 Nm^3/hr (0.16 MW equiv) unit treating flue gas from an oil-fired boiler. A larger pilot plant treating 5000 Nm^3/hr (1.6 MW equiv) of flue gas from an oil-fired boiler, containing 1150 ppm SO_2 and 180 ppm NO_x , has been operating since September 1975. Over a long-term (3000 hr) continuous operation the SO_2 and NO_x removal efficiencies in this pilot plant averaged 90 and 80% respectively.

It has recently been reported (95) that IHI is testing their process on a 27,000 Nm^3/hr (9 MW equiv) prototype unit at Tokyo Shibaura Electric Company near Tokyo. Additional information has not been published.

IHI is now working toward reducing the costs associated with the generation of O_3 and also the development of an effective but inexpensive method of treating wastewater from their process.

This process has not been tested on flue gas from a coal-fired boiler. The next development step for the IHI process would be to demonstrate the long-term reliability of this system in their prototype unit. The ability of this process to handle coal-fired flue gas also needs to be demonstrated.

Background of Process Developer

IHI is a relatively large Japanese shipbuilding and metal fabricating company which entered the air pollution control field in the early 1960's. IHI is a leading manufacturer and marketer of ESP, TCA, and complete FGD units in Japan. The total SO_2 removal plant capacity built by IHI in the last 5 yr is approximately 10 million Nm^3/hr (3300 MW equiv) with about 50% based on the wet lime-limestone- $CaSO_4 \cdot 2H_2O$ recovery system.

No American company has yet been licensed by IHI to market their process in the U.S. However IHI has a subsidiary, Ishikawajima-Harima Heavy Industries, Inc., in New York City (branch offices in San Francisco and Houston), through which inquiries about this process are handled.

Published Economic Data

The following total capital investment and annual revenue requirements are based on economic data provided by IHI for treating flue gas from an oil-fired boiler (1500 ppm SO_2 , 180 ppm NO_x , and 0.1 g/ Nm^3 of dust). Assuming SO_2 and NO_x removal efficiencies of 90 and 80%, respectively, the total capital investment for a 500,000 Nm^3/hr (167 MW equiv) unit is estimated (117) at 4,200 million yen and the revenue requirement is estimated at 8,200 yen/kl of oil (construction basis: Japan and 1976 costs). If 300 yen/\$ and 3000 $Nm^3/hr/MW$ equiv are assumed, these values correspond to a capital investment of \$84/kW of installed capacity and revenue requirement of 6.8 mills/kWh.

Raw Material, Energy, and Operation Requirements

Assuming the same basis as was given above for the published economic data, i.e., 500,000 Nm^3/hr of oil-fired flue gas containing 1,500 ppm SO_2 and 180 ppm NO_x and removal efficiencies of 90% for SO_2 and 80% for NO_x , the raw material requirements would be:

<u>Raw material</u>	<u>Quantity</u>
$CaCO_3$	3.5 tons/hr (short tons)
H_2SO_4	396 lb/hr
Slaked lime $[Ca(OH)_2]$	352 lb/hr
Additives	154 lb/hr

The utility requirements under these same conditions would be:

<u>Utility</u>	<u>Quantity</u>
Electricity	8,400 kW
Fuel oil	4,675 lb/hr
Steam	9,460 lb/hr
H ₂ O	240 gpm

This quantity of electricity represents approximately 5% of the generating capacity of the boiler. For treating flue gas containing 2400 ppm SO₂ and 600 ppm NO_x, the electrical requirements have been estimated (117) as about 9.2% of the boiler generating capacity.

The operating personnel needed for the IHI processes are nine men per day.

The maintenance requirements for this process have not been published.

Technical Considerations

The IHI simultaneous SO₂-NO_x removal process, since it is very similar to the other wet, oxidation-absorption-reduction processes, will have the same process control problems. The major control problem will be the O₃ generation and injection system since O₃ is extremely reactive and cannot be stored economically. As the amount of O₃ injected falls below the stoichiometric amount required, the NO_x removal efficiency gradually drops from 80-85% until the NO_x removal efficiency reaches approximately 5% when no O₃ is injected. Increasing the amount of O₃ injected above the stoichiometric amount sharply increases the operating costs for this system, since the cost of O₃ generation represents a substantial portion of the operating costs for this system.

The SO₂ removal efficiency is insensitive to the inlet flue gas composition and will remain over 90% under reasonable absorber operating conditions. The overall design of the system is very similar to a conventional FGD system with a L/G ratio in the absorber of about 10-12 l/Nm³ (60-75 gal/kuft³ at 127°F).

The NO_x removal efficiency is also relatively insensitive to the inlet flue gas composition provided that the mol ratio of SO₂ to NO_x in the flue gas remains greater than 2.5. Although not mentioned by IHI, this ratio was assumed since this process, at least in the absorption step, is nearly identical with other oxidation-absorption-reduction processes, which operate under similar conditions and apparently by the same mechanisms. This relatively high mol ratio is required since the absorbed SO₂, in the form of the SO₃⁻ ion, is used to reduce the absorbed NO_x. When the SO₂-NO_x mol ratio in the flue gas falls below 2.5:1, insufficient amounts of the SO₃⁻ ion are available to reduce the NO_x and the NO_x removal efficiency will drop below 80-85%.

During bench-scale testing, a spray tower was used as an absorber and the NO_x removal efficiency as a function of various absorber parameters and scrubbing solutions was studied. Initially a comparison of Na_2SO_3 versus CaSO_3 was made with the result being that the NO_x removal efficiency of a 5% Na_2SO_3 solution was approximately 70%, whereas the efficiency of a 5% CaSO_3 slurry was only about 20%. (Although not mentioned by IHI, this large difference in NO_x removal efficiency is probably due to the differences in the solubility of this SO_3^{2-} in the scrubbing solution.) However, by simply adding a small amount (0.01-0.02 mol/l) of CuCl_2 mixed with either NaCl or calcium chloride (CaCl_2) (0.17 mol/l) to the scrubbing solution, the NO_x removal efficiency can be sharply increased to 80-90%. From these studies by IHI it is apparent that the addition of an O_3 generation and an H_2O -soluble catalyst to a conventional limestone FGD system will result in a feasible simultaneous SO_2 - NO_x system.

One of the most important operating parameters for this process is the L/G ratio in the absorber. From preliminary pilot-plant tests conducted by IHI, Figure 14 shows a comparison of the NO_x removal efficiency as a function of the L/G ratio in the absorber. For 80-90% NO_x removal an absorber L/G ratio in the range of 10-12 l/Nm^3 (60-75 gal/kft³ at 127°F) will be required.

Although this process has not been tested on flue gas from a coal-fired boiler, the only two major technical considerations in adapting this system for treating flue gas from a coal-fired boiler would be the addition of a closed-loop prescrubber section to remove the increased particulate and Cl^- loadings associated with coal combustion and secondly, what type of H_2O treatment system would be required to prevent the discharge of excess N compounds in the wastewater. Although IHI estimates only a small amount of NO_3^- is formed, that statement is based on NO_x concentrations of 100-200 ppm instead of the 600 ppm or higher NO_x levels which are associated with coal-fired flue gas. This, of course, also leads to economic considerations in converting this process to treating coal-fired flue gas since a wastewater treatment section will probably be required and this will increase the costs for the process. In addition, tripling the NO_x levels will approximately triple the O_3 generation costs and, since the cost of O_3 is one of the major operating costs associated with this process, this high concentration of NO_x will also increase the annual operating costs.

Recently published information for their 5000 Nm^3/hr pilot plant suggests that IHI has modified the regeneration section of this process to eliminate this potential wastewater problem. Apparently after the byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been removed in the centrifuge, the remaining liquid is evaporated at 90°C (194°F) to form a solid mixture of $\text{Ca}(\text{NH}_2\text{SO}_3)_2$, CaSO_4 , CuCl_2 , and CaCl_2 . This mixed salt product is then conveyed to a thermal decomposer operating at 900°C (1650°F) where the $\text{Ca}(\text{NH}_2\text{SO}_3)_2$ is decomposed into CaSO_4 and molecular N_2 . Detailed information on this new regeneration scheme has not been made available.

As with the other wet simultaneous removal processes, retrofitting this system on existing power plants would be relatively easy if sufficient land is available nearby for siting the various process equipment. The major modification to the existing plant would be the installation of a common

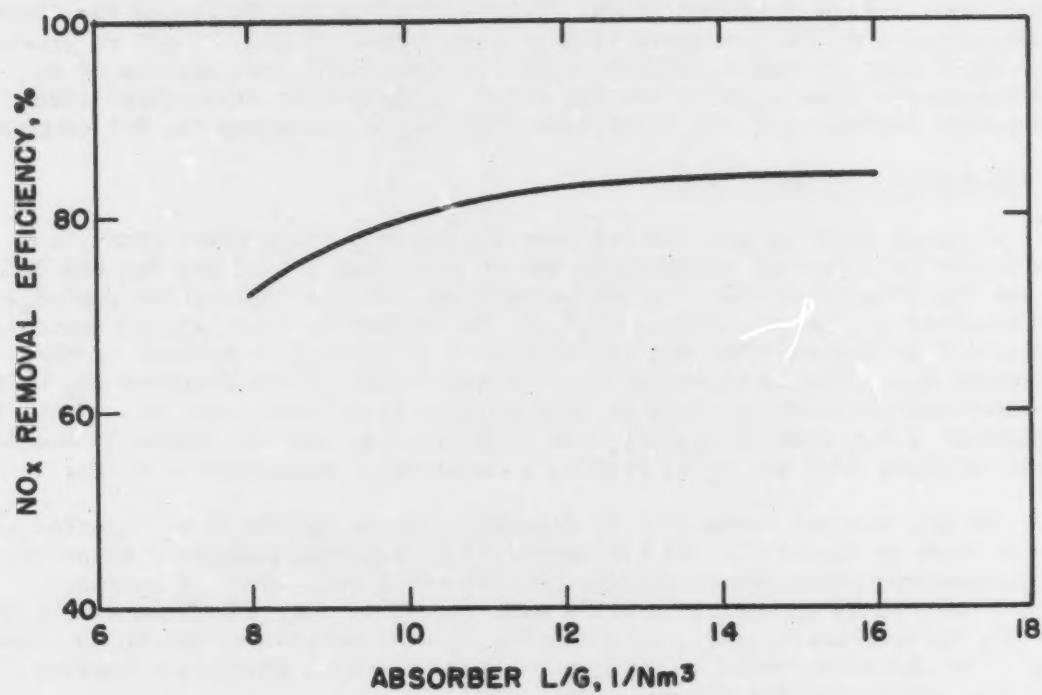


Figure 14. Effect of Absorber L/G on NO_x Removal Efficiency for IHI Process (60).

plenum from the boilers or the ESP to feed the four scrubber trains on a 500-MW boiler. The existing cold ESP could be removed and replaced with the venturi-type prescrubbers to remove the Cl^- as well as the flyash from the flue gas. The use of a common plenum and four absorber trains will allow this system to cycle with the boiler by simply closing off any combination of trains. The O_3 generation section can also be easily turned down since this section is made up of a battery of small O_3 generators, any combination of which can be shut down independently.

Most of the process equipment and piping for this process will need to be elastomer-lined carbon steel to prevent the corrosion and erosion problems associated with handling circulating limestone slurries and Cl^- solutions. Exceptions to this elastomer lining include the flue gas ducts and the thermal decomposer. The flue gas ducts will be constructed of Inconel 625 to prevent both H_2SO_4 mist corrosion and the oxidation associated with the use of O_3 . The decomposer will probably require either stainless or glass-lined steel due to the extreme reaction conditions required to decompose the N-S compounds.

Environmental Considerations

Although this process has not been tested in a large pilot plant, the developers believe this process can remove more than 90% of the SO_2 and 80% of the NO_x from oil-fired flue gas containing 1000 ppm SO_2 and 200 ppm NO_x . The absorbed SO_2 is oxidized to SO_4^{2-} and is removed as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Approximately 80% of the absorbed NO_x is reduced to $\text{Ca}(\text{NH}_2\text{SO}_3)_2$ with most of the remainder converted to molecular N_2 . However, some of the absorbed NO_x will be converted to $\text{Ca}(\text{NO}_3)_2$ which is very soluble in aqueous solution. These N compounds, i.e., both $\text{Ca}(\text{NH}_2\text{SO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$, can then be thermally decomposed to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and N_2 to prevent a significant wastewater problem.

The NO_x removal efficiency is dependent on the amount of O_3 injected as can be seen in Figure 15. As the amount of O_3 injected decreases below the stoichiometric requirement, the NO_x removal drops below 85%. A complete failure of the O_3 generation section will result in only approximately 5% of the NO_x being removed (i.e., only the NO_x already present as NO_2 in the flue gas). On the other hand, a complete failure of the O_3 generation section will not affect the SO_2 removal efficiency.

The O_3 used to oxidize the NO in the flue gas is a very strong oxidizing agent and hence, even at low concentrations, it presents a significant work hazard for this process.

Critical Data Gaps and Poorly Understood Phenomena

The critical data gaps for this process included:

1. Stream compositions and operating conditions in each piece of process equipment
2. The maintenance requirements for the IHI process
3. Reactions and mechanisms in the decomposer

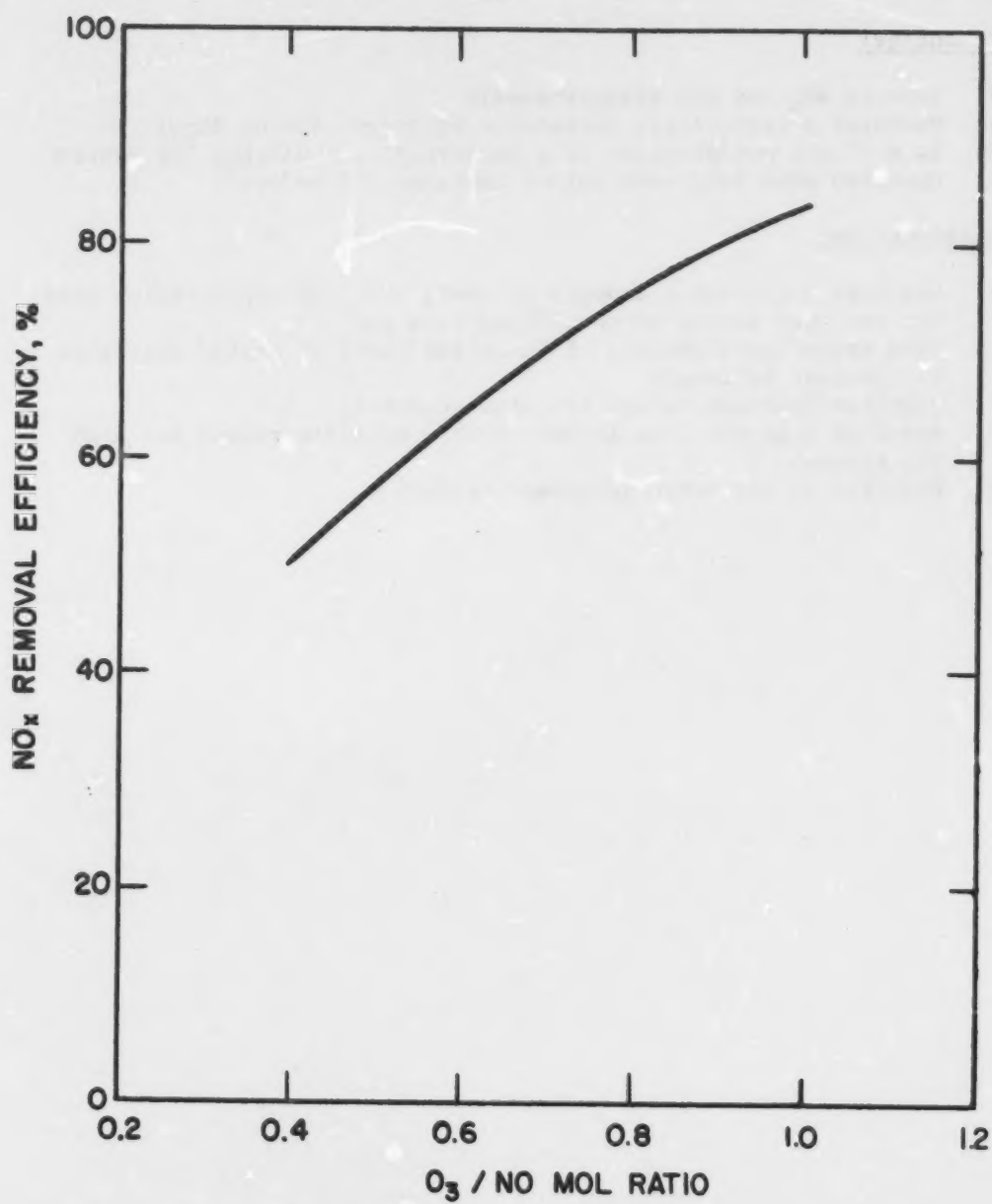


Figure 15. Effect of Ozone/NO Mol Ratio on the NO_x Removal Efficiency for IHI Process (60).

Advantages and Disadvantages

The major advantages and disadvantages of the IHI process are listed below.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Produces a potentially marketable byproduct ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
3. Is a slight modification of a commercially available FGD system
4. Operates with full particulate loadings ($>7 \text{ gr/sft}^3$)

Disadvantages

1. Requires significant amounts of energy for the regeneration step
2. Has not been tested on coal-fired flue gas
3. Uses significant amounts of stainless steel or exotic materials for process equipment
4. Requires flue gas reheat for plume buoyancy
5. Requires flue gas constituents within specific ranges for high NO_x removal
6. Requires an expensive gas-phase oxidant

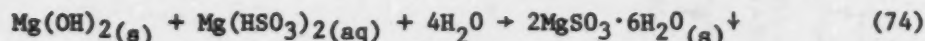
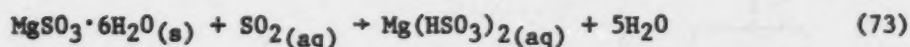
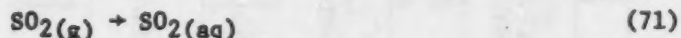
KAWASAKI HEAVY INDUSTRIES MAGNESIUM PROCESS - WET, OXIDATION-ABSORPTION
(NO_x-SO_x)

Process Description and Principles of Operation (65, 66)

This process, which was developed by Kawasaki Heavy Industries, is a wet "simultaneous" SO₂-NO_x process using a magnesium hydroxide $\overline{\text{Mg(OH)}_2}$ slurry and O₃ injection. This absorber is unique in that it is divided into three sections, one section for desulfurization, the second for denitrification based on equimolar NO-NO₂ absorption, and the third for further denitrification based on O₃ injection and NO₂ absorption. Without the third stage of absorption using O₃, NO_x reduction below 150-200 ppm is difficult to attain, while with O₃ injection 80-90% denitrification can be achieved. The overall efficiency depends on the O₃:NO ratio in the third section; the higher the O₃:NO ratio, the higher the overall removal efficiency. Since an NO_x removal efficiency of 90% is desirable, only the three-section absorber with O₃ injection will be considered. In addition to 90% NO_x removal, this process is also able to remove more than 95% of the SO₂ in the flue gas.

The Kawasaki process consists of five major sections including (1) gas-phase oxidation, (2) absorption of SO₂ and NO_x, (3) regeneration and oxidation of recycle NO, (4) CaSO₄·2H₂O production, and (5) regeneration of absorbent $\overline{\text{Mg(OH)}_2}$. The overall process outline is shown in the flow diagram in Figure 16.

The flue gas from the air heater passes countercurrently to an Mg(OH)₂ slurry in the first, or desulfurization, section of the absorber. As the flue gas passes through this section, the gas is cooled and humidified as the SO₂ is stripped from the flue gas and subsequently enters the absorbing solution. During this absorption, the SO₂ undergoes the following reactions:



The liquid effluent from this desulfurization section is pumped to a liquid holding tank while the flue gas enters the first of two denitrification sections in the absorber.

In the first denitrification stage of the absorber, the flue gas is mixed with a recycle NO₂ stream to adjust the mol ratio of NO to NO₂ to 1. As the flue gas passes countercurrently to an Mg(OH)₂ slurry, equimolar amounts of NO and NO₂ are absorbed and converted according to the following reactions:

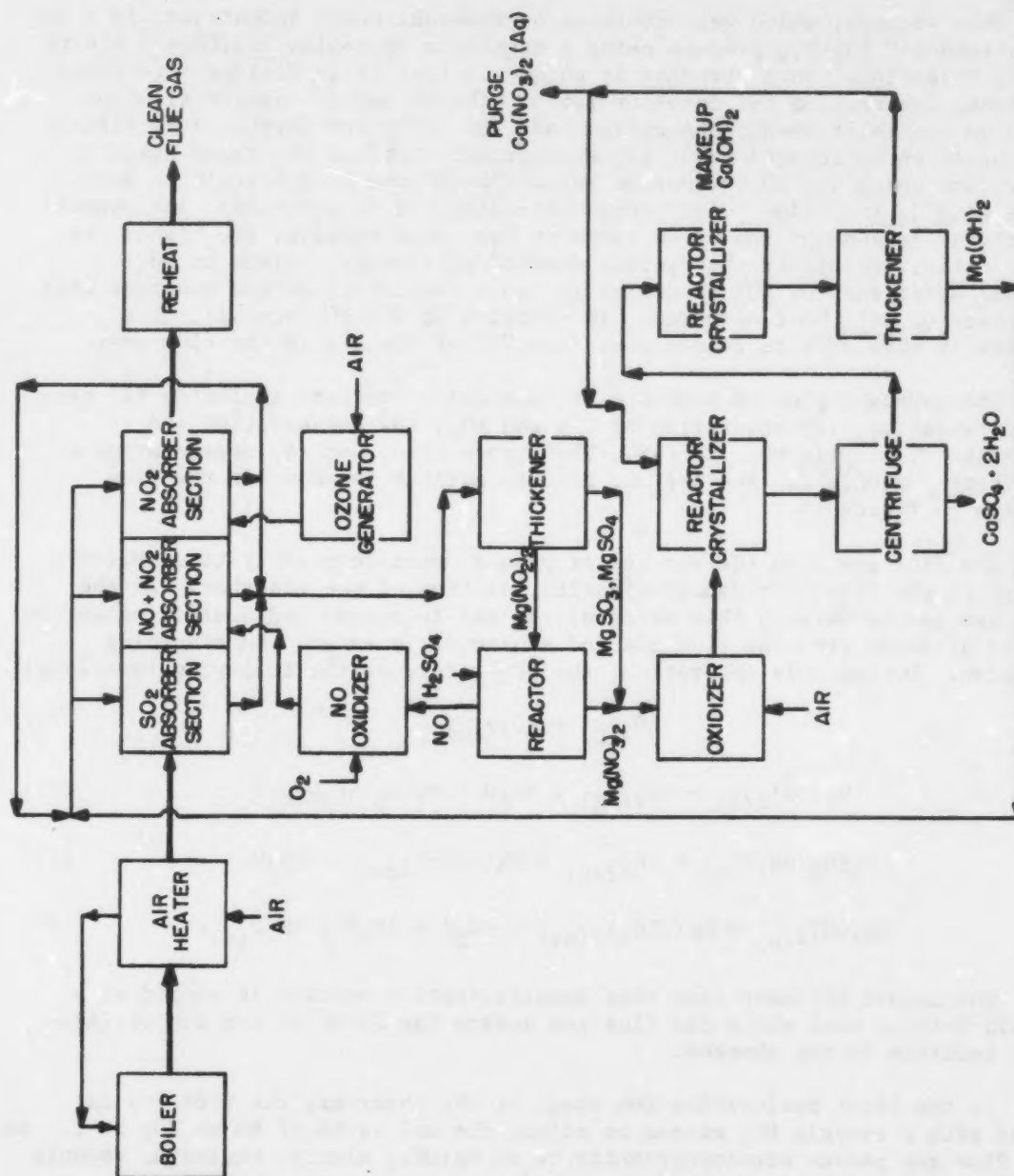
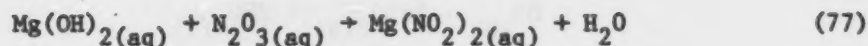
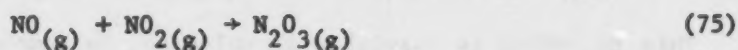
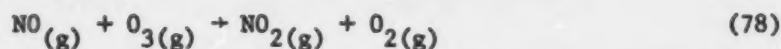


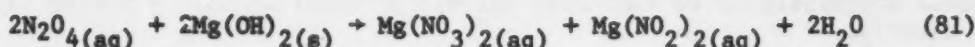
Figure 16. Flow Diagram of Kawasaki Heavy Industries Process.



As the concentration of NO_x in the flue gas decreases below about 200 ppm, the rate of reaction (75) decreases and becomes negligible and the remaining NO_2 is absorbed by reactions (79), (80), and (81), shown below. Further NO_x reductions below 150-200 ppm require the use of O_3 and a separate denitrification stage. The liquid effluent from this first denitrification stage is sent to the absorber holding tank and mixed with the effluent from the desulfurization section, while the flue gas containing 150-200 ppm NO_x passes overhead and is injected with O_3 to oxidize NO to NO_2 before entering the second denitrification section.



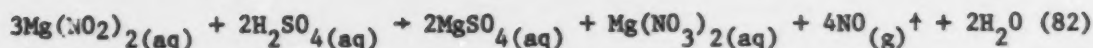
The flue gas then passes countercurrently to an Mg(OH)_2 slurry in the second denitrification stage of the absorber where the NO_2 undergoes the following reactions:



The liquid effluent from this denitrification stage is split into two streams—one stream is recycled to feed liquid solution to each section of the absorber while the other enters the holding tank below the absorber and is mixed with the effluent from each of the other two sections of the absorber.

The scrubbing solution in the holding tank thus contains both dissolved NO_2^- and NO_3^- salts and a slurry of SO_3^- and SO_4^- and is pumped to the regeneration section.

The first stage of the regeneration section consists of a thickener to separate the soluble magnesium nitrites $\text{Mg(NO}_2)_2$ and nitrates $\text{Mg(NO}_3)_2$, which are removed in the thickener overflow, from the insoluble SO_3^- and SO_4^- , which are taken out in slurry form from the bottom of the thickener. The thickener overflow containing the mixed NO_2^- and NO_3^- salts is pumped to a reactor where the NO_2^- is decomposed by the addition of H_2SO_4 according to the following reaction:

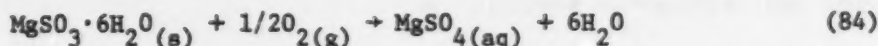


This NO, which is insoluble in solution, is removed as a gas stream and is passed through an oxidation tower where the NO is oxidized in air to form NO₂.

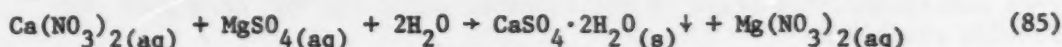


This NO₂ is then injected into the flue gas prior to the first denitri-fication section of the absorber to adjust the ratio of NO:NO₂ to 1:1 and thus facilitate NO_x absorption by reactions (75), (76), and (77).

The liquid effluent from the NO₂⁻ decomposition reactor, containing magnesium sulfate (MgSO₄) and Mg(NO₃)₂ is mixed with the SO₃⁼ slurry bottoms from the thickener and sent to a second oxidizing tower where an air stream is used to oxidize the magnesium sulfite (MgSO₃·6H₂O) to MgSO₄.

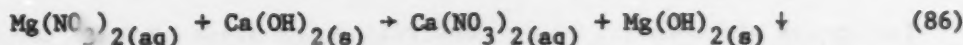


The MgSO₄ removed from the oxidizing tower is further treated with Ca(NO₃)₂ in a double decomposition reactor to produce CaSO₄·2H₂O and Mg(NO₃)₂.

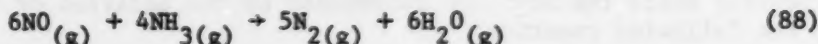


The resulting CaSO₄·2H₂O slurry is pumped to a centrifuge where the CaSO₄·2H₂O is removed and sent to a byproduct storage area.

The centrate, containing mainly Mg(NO₃)₂, is converted in a second double decomposition to insoluble Mg(OH)₂ by reaction with a makeup slurry of Ca(OH)₂.



After separating this Mg(OH)₂ as a slurry product from the bottom of a second thickener, the Mg(OH)₂ is recycled back to the absorber. The over-flow from the thickener, containing mainly Ca(NO₃)₂, is split into two streams: one for recycle to the CaSO₄·2H₂O production reactor and the other to a byproduct recovery section. It is hoped by the developers that, by concentrating this Ca(NO₃)₂ byproduct stream, it can be sold as a low-grade liquid fertilizer. If this Ca(NO₃)₂ cannot be sold as is, the developers suggest decomposing this Ca(NO₃)₂ into CaO and NO which will then be reduced with NH₃, i.e.,



Although this series of process steps is technically feasible, the high temperatures and complicated process equipment requirements would make this process expensive.

Other possible solutions to the $\text{Ca}(\text{NO}_3)_2$ problem would be either evaporation and disposal in a landfill or biological treatment in a series of holding ponds. These would be expensive alternatives and hence disposal of the $\text{Ca}(\text{NO}_3)_2$ as a liquid fertilizer, whether sold as a byproduct or given away, would be a more suitable solution.

Status of Development

The absorption section of the Kawasaki simultaneous SO_2 - NO_x process was first tested in a bench-scale unit treating $100 \text{ Nm}^3/\text{hr}$ (0.03 MW equiv) of flue gas from an oil-fired boiler. However, high denitrification efficiencies were not attainable using only equimolar absorption and therefore testing was begun in March 1974 using O_3 for the gas-phase oxidation of NO .

This resulting process was scaled up to treat $5000 \text{ Nm}^3/\text{hr}$ (1.6 MW equiv) of flue gas from a coal-fired boiler in June 1975. Very little data have been published concerning the operation of this pilot plant.

Background of Process Developer

Kawasaki is a large, diversified Japanese company with extensive previous experience in air pollution control technology. This involvement began in 1968 with the start of research aimed at the development of an FGD system. Initial work on an FGD system included studying an Mg scrubbing-regeneration process, an Na scrubbing process, and a Ca scrubbing process. Approximately seven prototype units using the Na scrubbing system and two of the Ca-based scrubbing systems were completed between 1973 and 1975.

In 1971 Kawasaki entered into an agreement with Kureha Chemical Industry Company for the joint development of the Na_2SO_3 - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ double-alkali FGD system. Three commercial units based on this technology are now operating and two more commercial units are under construction.

The development work for their $\text{Mg-CaSO}_4 \cdot 2\text{H}_2\text{O}$ double-alkali FGD process was begun in 1972 with scaleup to a pilot-plant unit in early 1975. Two commercial plants based on the $\text{Mg-CaSO}_4 \cdot 2\text{H}_2\text{O}$ system were completed and began operating in 1976.

No American company has been licensed by Kawasaki to market their process in the U.S. However, Kawasaki does have a liaison office in New York City through which inquiries about their process are handled.

Published Economic Data

Neither the estimated total capital investment nor the annual revenue requirements for the Kawasaki simultaneous SO_2 - NO_x process has been published.

Raw Materials, Energy, and Operation Requirements

The major raw material requirements for this process will include limestone (or lime) to remove the SO_4^{2-} as byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, H_2SO_4 for the decomposition of $\text{Mg}(\text{NO}_3)_2$, and lesser amounts of $\text{Mg}(\text{OH})_2$ to replace Mg losses throughout the system. The quantities of these raw materials required have not been published.

The major energy requirements for this system will include fuel oil for flue gas reheat and electrical energy for both O_3 generation and process equipment operation. Other utilities would include cooling and makeup H_2O . These utility requirements have not been published.

The operating manpower and maintenance requirements for this system have not been made available.

Technical Considerations

The Kawasaki process, with its extensive equipment requirements and O_3 generation section, will be one of the more complex processes and hence one of the most difficult to control. The major control problems will be the absorber since it is apparently split into three separate scrubbing sections in series with three different liquid feed streams and each section operating under different absorption conditions. Controlling the O_3 system will also be relatively easy since the amount of O_3 required in the second denitrification section will be relatively constant regardless of the inlet flue gas composition.

The SO_2 removal efficiency is insensitive to the inlet flue gas composition since the first section of the absorber is essentially a conventional Mg FGD scrubber and it is followed by two other absorber sections using an Mg slurry. Thus the desulfurization efficiency should be consistently over 95%.

The NO_x removal efficiency should also be insensitive to the inlet flue gas composition since the NO is not reduced by the SO_3^{2-} ion as in other wet processes but are simply oxidized and removed as NO_3^- ions in the wastewater.

As mentioned above, from the limited amount of information available at the present time, it appears likely that each of the three sections of the absorber operate under slightly different conditions. The desulfurization section of the absorber operates at an L/G ratio of 5 l/Nm^3 (31 gal/kaft^3 at 127°F) and a pressure drop of $150 \text{ mm H}_2\text{O}$ to give an SO_2 removal efficiency of 95%. The second, or equimolar NO- NO_2 absorption section, operates at an L/G ratio of about 10 l/Nm^3 (65 gal/kaft^3 at 127°F) and removes 40-50% of the incoming NO_x . The third, or NO_2 absorption section, also operates at an L/G ratio of about 10 l/Nm^3 but the NO_x removal efficiency in this section is a function of the $\text{O}_3:\text{NO}$ ratio. Under the L/G ratio specified above and an $\text{O}_3:\text{NO}$ ratio of 1.4, approximately 85% of the remaining NO_x can be removed. Therefore, an overall NO_x removal efficiency of about 90% can be attained.

At the present time the actual design of the absorption section is not particularly clear especially for larger prototype units. Since the three sections of the absorber are physically separated from each other and each section is estimated to be approximately the same size as a conventional Mg FG scrubber, when this process reaches a commercial size more than one absorber in each train may be necessary. The increased cost of such a system would probably make this process very expensive.

The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ byproduct stream would be contaminated with various NO_3^- and SO_3^{2-} salts and hence would probably not be marketable in the U.S. where high-quality natural $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is readily available. The cost of upgrading this $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ would further increase the cost of this already expensive process and therefore most of this $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will probably be used as a landfill material.

The wastewater purge stream containing a relatively high NO_3^- concentration will require some sort of treatment, either biological treatment or evaporation to prevent secondary water pollution. Kawasaki has not specified as yet what type of H_2O treatment will be used.

Since this is a wet process, retrofitting this system on a conventional coal-fired power plant will be relatively simple providing sufficient land is available nearby for both the extensive process equipment requirements and a wastewater treatment section. The major modification would be the removal of the cold ESP and the installation of a common plenum to distribute the flue gas from the boiler to the four scrubber trains. This design will also allow the removal system to cycle with the boiler by simply closing off various combinations of scrubber trains.

Most of the process equipment and piping will be elastomer lined to prevent the corrosion and erosion problems associated with the circulation of Mg slurries. The only exceptions to this elastomer lining are the flue gas ducts, which will be made of Inconel 625, and the decomposition reactor which will be made of stainless or glass-lined steel.

Environmental Considerations

During pilot-plant (1.7 MW equiv) testing on flue gas from a coal-fired boiler containing 1000 ppm SO_2 and 200-400 ppm NO_x , the Kawasaki Mg process was able to maintain 95% SO_2 removal and approximately 50% NO_x removal at an L/G ratio of 10 l/Nm³ (85 gal/kaft³ at 127°F) without the addition of O_3 . If O_3 is added to the third stage absorber to oxidize NO to NO_2 , the NO_x removal can be increased to 80% removal at an O_3 :NO ratio of 1.3 and 90% removal at a ratio of O_3 :NO of 1.4.

The SO_2 absorbed from the flue gas is air-oxidized to SO_4^{2-} and removed as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The equimolar mixture of NO and NO_2 is absorbed into the slurry to form NO_2^- salts, converted to NO_3^- salts, and removed as $\text{Ca}(\text{NO}_3)_2$. Unless this weak $\text{Ca}(\text{NO}_3)_2$ solution can be sold as a low-grade fertilizer,

further processing, either by evaporation to solid $\text{Ca}(\text{NO}_3)_2$ or denitrification by biological treatment, will be required to prevent secondary water pollution from this stream.

Since this process does not use the SO_2 absorbed from the flue gas to reduce NO_x , there is no theoretical minimum $\text{SO}_2:\text{NO}_x$ ratio in the flue gas as in most of the other wet simultaneous removal processes.

The generation and use of O_3 in this process presents a significant hazard of workers in this plant. O_3 is a very strong oxidizing agent and can have significant effects on the health of workers even in relatively low concentrations.

Critical Data Gaps and Poorly Understood Phenomena

Listed below are the major data gaps for the Kawasaki process.

1. Operating conditions for each piece of equipment
2. Stream compositions throughout the system
3. Estimated capital investment and revenue requirements
4. Raw material, energy, and operation requirements
5. Conversion in the various oxidizers and reactors
6. Type and diagram of particular removal system for coal-fired applications
7. Type and diagram of wastewater $[\text{Ca}(\text{NO}_3)_2(\text{aq})]$ treatment section

The entire absorber section is not well understood at the present time. The single absorber in the pilot plant is apparently internally split into three sections with countercurrent gas-liquid flow, but when this pilot plant is scaled up to a prototype or commercial unit three separate absorbers connected in series may be required for each scrubber train. For the four scrubber trains on a 500-MW plant this would mean a total of 12 absorbers the size of a conventional Mg FGD scrubber. Further complicating this section is that the total liquid effluent from the first two sections of the absorber apparently passes through the regeneration section.

Advantages and Disadvantages

By virtue of the fact that this process is a wet simultaneous $\text{SO}_2\text{-NO}_x$ process using modified gas-phase oxidation, it has certain advantages and disadvantages, as listed below, over other types of flue gas denitrification systems.

Advantages

1. Achieves >95% SO_2 removal efficiency
2. Produces a potentially marketable byproduct ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
3. Has been tested on coal-fired flue gas on pilot-plant or greater scale
4. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

1. Forms secondary source of pollution (wastewater NO_3^- salts)
2. Has not been operated for a long-term continuous period
3. Incorporates design features which may present significant process control problems
4. Uses significant amounts of stainless steel or exotic materials for process equipment
5. Has a high L/G ratio in the absorber ($>70 \text{ gal/kaft}^3$)
6. Requires flue gas reheat for plume buoyancy
7. Requires an expensive gas-phase oxidant

KOBE STEEL PROCESS - WET, ABSORPTION-OXIDATION ($\text{NO}_x\text{-SO}_x$)

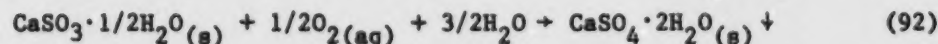
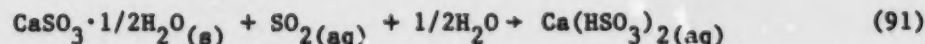
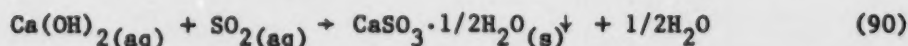
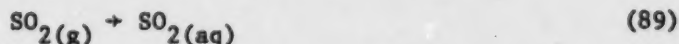
Process Description and Principles of Operation (5, 43)

In addition to their dry, SCR process, Kobe Steel, Ltd., has also been developing a wet process to remove NO_x . Although very little information has been published as yet, this NO_x process is a wet, absorption-oxidation process; that is, the NO_x is absorbed into the scrubbing solution as NO and oxidized by $\text{Ca}(\text{ClO})_2$ to form NO_3^- salts. The use of a liquid-phase oxidant, however, requires two separate absorbers for desulfurization and denitrification to prevent the reaction of $\text{Ca}(\text{ClO})_2$ with SO_2 and thus the excessive consumption of this expensive oxidizing agent. The SO_2 absorbed in the separate FGD scrubber is oxidized to SO_4^{2-} and removed as byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The Kobe Steel CAL- NO_x process is composed of six major sections including (1) prescrubbing, (2) SO_2 absorption, (3) NO_x absorption, (4) chlorine (Cl_2) absorption, (5) NO_3^- decomposition, and (6) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ recovery. A more detailed outline of this process can be seen in the block flow diagram in Figure 17.

Although not mentioned by Kobe Steel the flue gas from a coal-fired boiler will probably require a closed-loop prescrubbing section to remove the increased particulates and Cl^- levels associated with coal combustion before entering the absorption section. In addition to removing 90% of the particulates and essentially all of the Cl^- , the prescrubber adiabatically humidifies and cools the flue gas from 150°C (300°F) to 53°C (127°F). The scrubbing solution from the base of the prescrubber flows to a holding tank from which most of the solution is recirculated through the prescrubber after makeup H_2O has been added. The remaining portion of the solution is removed as a purge stream to prevent the buildup of Cl^- and ash and is probably centrifuged to remove the ash from the Cl^- solution. This Cl^- solution would then be mixed with the purge stream from the absorption section before final treatment.

After passing through a mist eliminator, the flue gas passes counter-currently to a CaCl_2 -lime slurry as in a conventional lime FGD system. The SO_2 is readily absorbed and undergoes the following reactions.



The scrubbing solution flows to a holding tank from which most of the liquid is recycled to the absorber. The remaining portion of the scrubbing solution is pumped to the Cl_2 absorber.

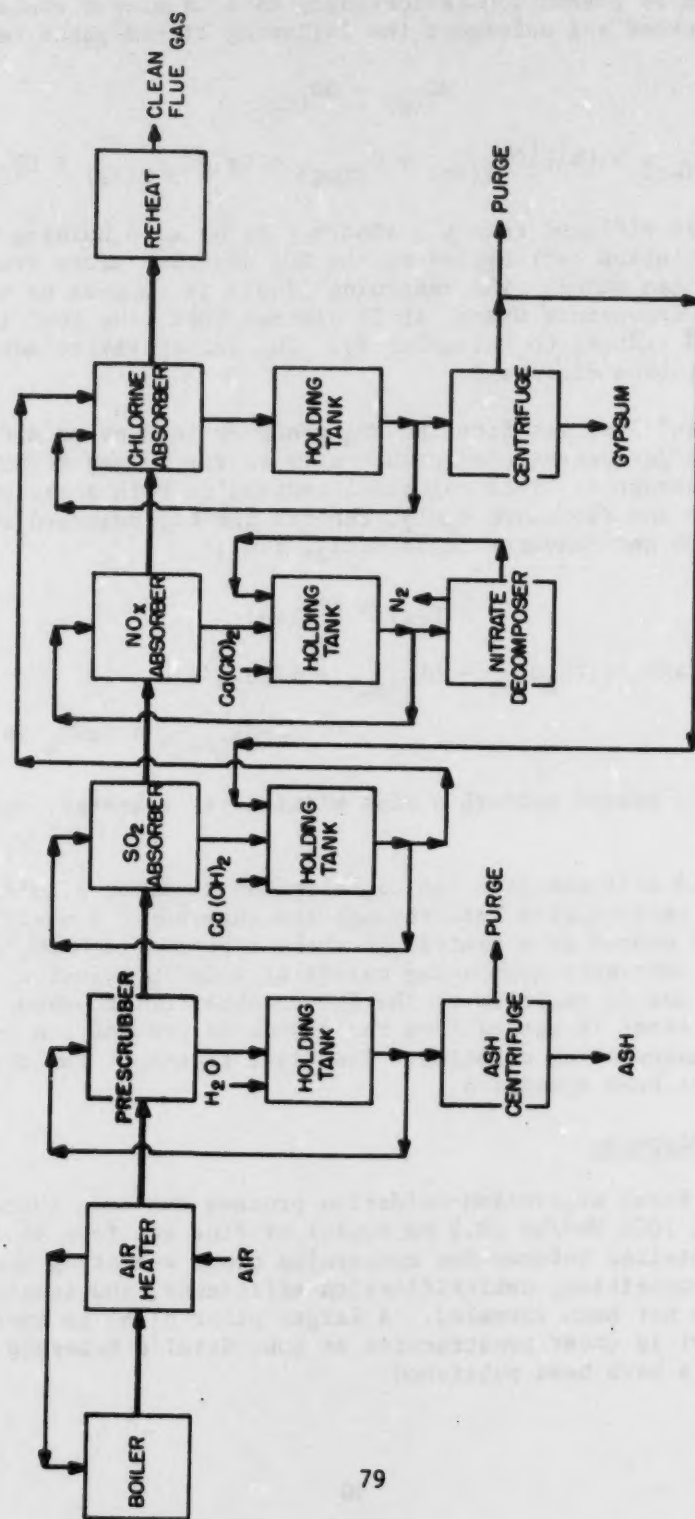
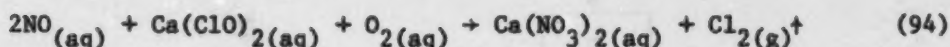


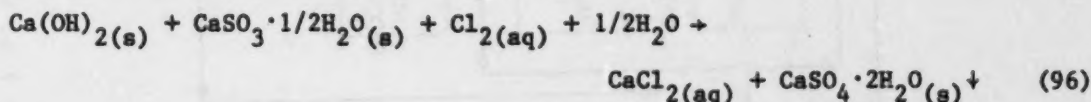
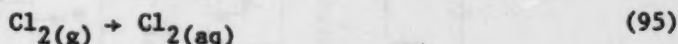
Figure 17. Flow Diagram of Kobe Steel Wet Process.

The flue gas from the FGD absorber is sent to the denitrification absorber where it passes countercurrently to a Ca slurry containing $\text{Ca}(\text{ClO})_2$. The NO is absorbed and undergoes the following liquid-phase reactions:



The liquid effluent from the absorber drops to a holding tank from which most of the solution is recycled to the NO_x absorber after fresh $\text{Ca}(\text{ClO})_2$ solution has been added. The remaining liquid is removed as a purge stream and sent to a decomposer where, it is claimed that, the NO_3^- is chemically decomposed and reduced to molecular N_2 . The decomposition method and reactions have not been disclosed.

The "clean" flue gas from the NO_x absorber is sent to a Cl_2 absorber in which the flue gas passes countercurrently to the purged scrubbing solution from the FGD absorber. This solution, containing both a mixture of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and dissolved CaCl_2 , absorbs the Cl_2 released when $\text{Ca}(\text{ClO})_2$ oxidizes the NO and converts it to CaCl_2 , i.e.,



The flue gas is passed through a mist eliminator, reheated, and sent to the stack.

The liquid effluent from the Cl_2 absorber drops to a holding tank and most of it is recirculated back through the absorber. A small purge stream is removed and pumped to a centrifuge where a byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ cake is removed. The centrate, consisting mainly of a CaCl_2 solution, is split into two streams: one is recycled to the FGD scrubber after makeup $\text{Ca}(\text{OH})_2$ is added and the other is purged from the system to prevent the buildup of Cl^- salts in the circulating solution. The final treatment for this solution, if any, has not been specified.

Status of Development

The Kobe Steel absorption-oxidation process has been tested on a pilot plant treating $1000 \text{ Nm}^3/\text{hr}$ (0.3 MW equiv) of flue gas from an iron-ore sintering plant. Detailed information concerning other operating parameters, such as flue gas composition, denitrification efficiency, and length of continuous operation, has not been revealed. A larger pilot plant to treat $50,000 \text{ Nm}^3/\text{hr}$ (16.7 MW equiv) is under construction at Kobe Steel's Kakogawa Mill but no further details have been published.

This process has not been tested on flue gas from a coal-fired boiler.

Recently Kobe Steel has stopped the development of this process and initiated studies into an entirely new wet denitrification process. However no information has been published as yet (43).

Background of Process Developer

Kobe Steel is a large Japanese corporation heavily involved in the iron and steel industry. With the coming of the strict air pollution regulations in Japan in the early 1970's, Kobe Steel entered the air pollution control field to solve the SO₂ emission problems from their plants. Their CAL-SO_x FGD system was developed and has been in commercial operation (50-120 MW equiv) since April 1976.

In response to increasingly strict NO_x regulations, Kobe Steel began the development of both a dry SCR process using NH₃ and a wet absorption-oxidation process for NO_x removal.

No American company has been licensed to market this technology in the U.S. However, Kobe Steel does have a liaison office in New York City through which inquiries about this process are handled.

Published Economic Data

Neither the estimated capital investment nor the annual revenue requirements has been published.

Raw Material, Energy, and Operation Requirements

The major raw material requirements for this process are lime for makeup slurry for the FGD absorber and Ca(ClO)₂ for the scrubbing solution in the NO_x absorber. No information has been made available on the quantities of lime and Ca(ClO)₂ required for this process.

The major energy requirements are fuel oil for reheating the flue gas and electricity for operating the process equipment. No information has been published on the quantities of energy required for this process.

The operating manpower and maintenance requirements have not been published.

Technical Considerations

The Kobe Steel wet process appears to be a relatively complex process with many pieces of process equipment including three absorbers and one prescrubber per train in the absorption section. The use of the liquid-phase oxidant would appear to be the most difficult process control problem but this would not be as difficult as using a gas-phase oxidant since Ca(ClO)₂ is relatively stable and could be stored in bulk quantities.

As is typical for absorption-oxidation processes, under normal circumstances, the NO_x removal efficiency is relatively insensitive to the inlet gas composition. The NO_x is absorbed and chemically converted to NO_3^- without reacting with SO_2 . This conversion to NO_3^- salts does require dissolved O_2 in the scrubbing solution but under normal boiler conditions enough O_2 is present in the flue gas for this reaction.

The desulfurization absorber is fed a lime slurry containing as its major constituent dissolved CaCl_2 . The operating conditions for this absorber have not been published but they would probably be the same order of magnitude as those in a conventional lime FGD system.

The operating parameters for the denitrification absorber and the Cl_2 absorber have not been published and hence only general comments can be made concerning their operation. Since NO is relatively insoluble in aqueous solutions, the NO_x absorbers must be extremely large with a high L/G ratio and low superficial gas velocity. The Cl_2 absorber would probably be much smaller since Cl_2 is relatively soluble in aqueous solution but no operating parameters have been assumed.

The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced as a byproduct will contain relatively high concentrations of CaCl_2 and $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ and hence the market value of this $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will probably be relatively low. The expense required to further purify this $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ would probably not be justified and thus the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ would probably be used as a landfill material.

Since this is a wet process, retrofitting this system on existing power plants should be relatively easy if sufficient land is available for siting the extensive process equipment required. The major modification would be the installation of a common plenum to connect the boilers to the four scrubber trains. This use of a common plenum will also allow this system to follow the boiler availability by simply closing off any combination of scrubber trains.

Except for the flue gas ducts which will be made of Inconel 625, the process equipment and piping for this system will be made of elastomer-lined carbon steel to prevent the pitting corrosion associated with circulating Cl^- solutions.

Environmental Considerations

No information is available on the sensitivity of either desulfurization or denitrification efficiencies to stoichiometry and operating conditions in the absorption section. The desulfurization section is essentially the Kobe Steel CAL- SO_x process which in other pilot plants has demonstrated >90% SO_2 removal. The SO_2 is absorbed to form SO_3^- , oxidized to SO_4^- , and removed as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The NO_x is absorbed as NO , oxidized to form NO_3^- , and chemically decomposed to yield molecular N_2 .

Critical Data Gaps and Poorly Understood Phenomena

Since only a minimal amount of information is available on the Kobe Steel wet process, detailing all of the critical data gaps and poorly understood phenomena would require an extensive list. Therefore, only the major data gaps have been listed below.

1. Stream compositions
2. Equipment operating conditions
3. Wastewater treatment section
4. Section for chemical decomposition of $\text{Ca}(\text{NO}_3)_2$
5. Raw material, energy, and operation requirements
6. Capital investment and annual operating cost
7. NO_x absorber and Cl_2 absorber operating conditions
8. Pilot-plant results
9. $\text{Ca}(\text{ClO})_2$ section (onsite generation or bulk storage)

Since there are so many critical data gaps it is difficult to specify any poorly understood phenomena other than the actual reactions involved in the absorption of NO_x . From previous studies the insolubility of NO , which represents 90-95% of all NO_x in the flue gas, has been overcome by either oxidizing the NO to NO_2 before absorption or adding a complexing agent to the scrubbing solution. Since this process oxidizes the NO after it has been absorbed into solution and no solution additive is mentioned, the actual mechanism of absorption is not clear.

Advantages and Disadvantages

The following list of advantages and disadvantages should be considered as being tentative and subject to revision as more information on the Kobe Steel process becomes available.

Advantages

1. Produces a potentially marketable byproduct ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
2. Operates with full particulate loadings ($>7 \text{ gr/sft}^3$)

Disadvantages

1. Forms secondary source of pollution (wastewater NO_3^- salts)
2. Has not been tested on coal-fired flue gas
3. Requires clean (SO_2 -free) gas feed
4. Has a low superficial gas velocity in the absorber ($<10 \text{ ft/sec}$)
5. Has a high L/G ratio in the absorber ($>70 \text{ gal/kaft}^3$)
6. Requires flue gas reheat for plume buoyancy
7. Requires an expensive liquid-phase oxidant

KUREHA PROCESS - WET, ABSORPTION-REDUCTION (NO_x - SO_x)

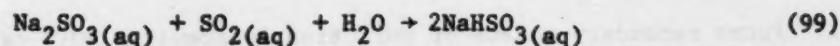
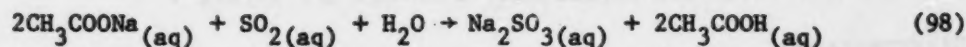
Process Description and Principles of Operation (61, 75)

The Kureha Chemical Industry Company, Ltd., process is similar to other absorption-reduction processes except that Kureha uses an Na_2SO_3 -acetic acid solution to simultaneously remove both SO_2 and NO_x . The absorber for this process is unique in that it is separated into two compartments, with the flue gas passing through each compartment. These compartments or stages include a simultaneous SO_2 - NO_x absorption section and an acetic acid removal section.

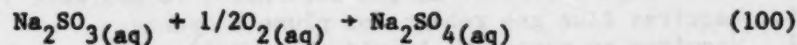
The overall process can be divided into six major sections including (1) prescrubbing, (2) absorption of both SO_2 and NO_x , (3) acetate recovery, (4) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production, (5) $\text{NH}(\text{SO}_3\text{Na})_2$ decomposition, and (6) NH_3 decomposition. The basic outline of this absorber and the associated process equipment is shown in the block flow diagram in Figure 18.

Although not mentioned by Kureha, the flue gas from the boiler air heater probably enters a closed-loop prescrubbing section which is assumed to remove 99% of the particulates and essentially all of the Cl^- from the flue gas before entering the absorption section. In addition, the prescrubber adiabatically humidifies and cools the flue gas from 150°C (300°F) to 53°C (127°F). The scrubbing solution drops into a holding tank from which most of the solution is recirculated through the prescrubber after makeup H_2O has been added. The remainder of the solution is removed as a purge stream and is pumped to a centrifuge to remove the flyash. Most of the centrate is recycled to the prescrubber holding tank, while a small purge stream is removed to prevent the buildup of Cl^- in the circulating solution.

The flue gas from the prescrubber enters the desulfurization section at the bottom of a perforated plate absorber. As the gas passes countercurrently to a sodium acetate (CH_3COONa) scrubbing solution, most of the SO_2 is rapidly stripped from the flue gas and undergoes the following reactions.



In addition to these primary reactions, the Na_2SO_3 also undergoes the following secondary reactions.



The NO_x , consisting primarily of NO , is relatively insoluble and is absorbed over the entire length of the absorber. This NO absorption is aided by an H_2O -soluble catalyst which is a proprietary Fe^{+2} chelating compound. The NO is absorbed and undergoes the following overall reactions.

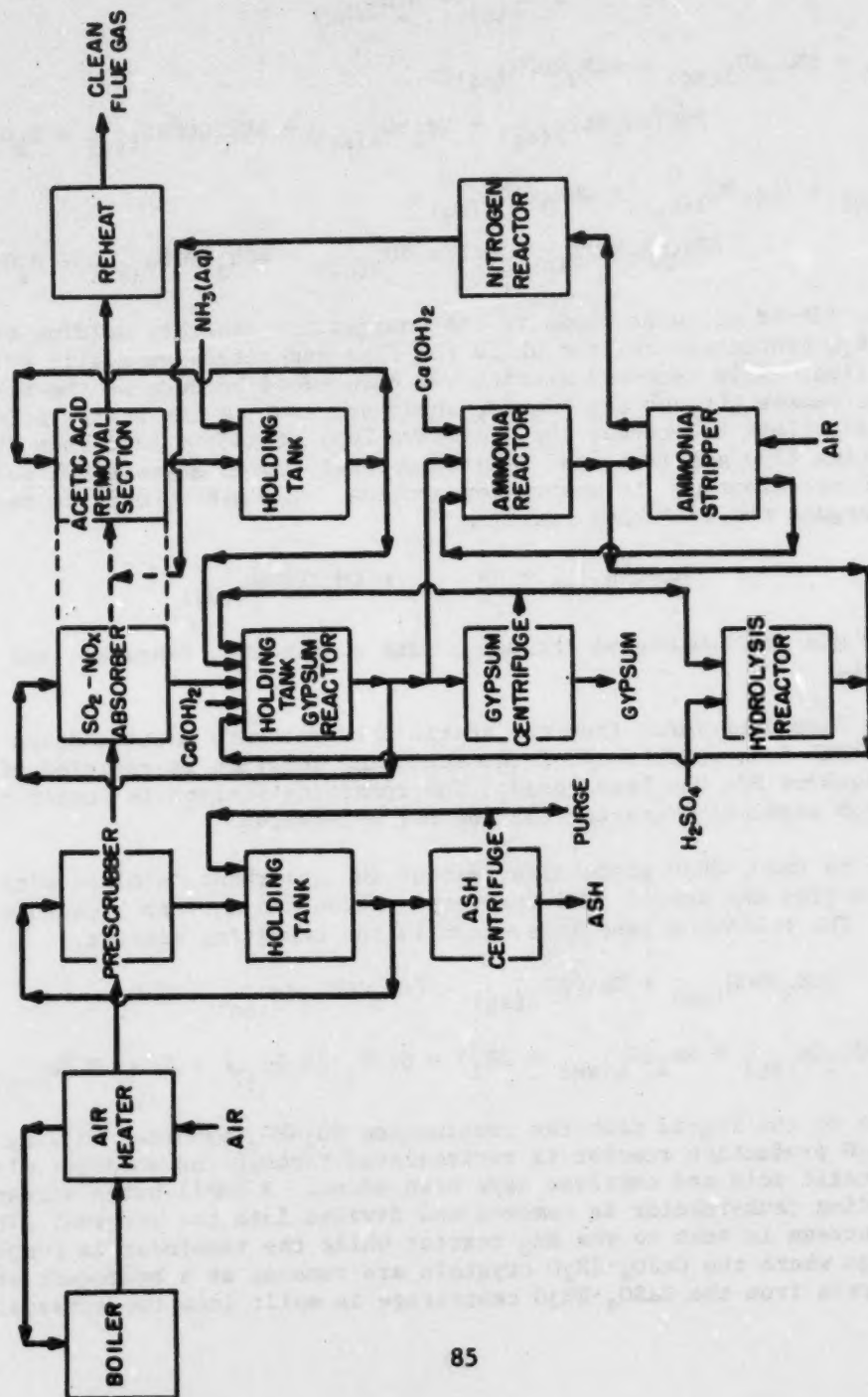
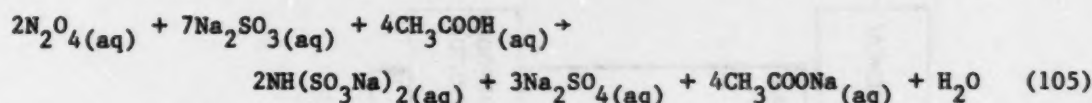
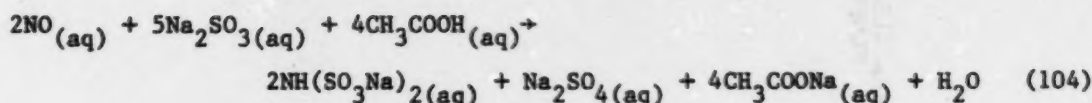
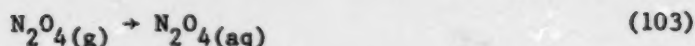
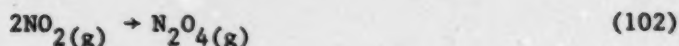
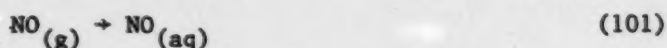
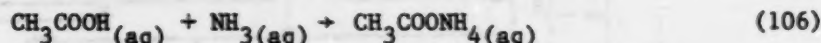


Figure 18. Flow Diagram of Kureha Wet Process.



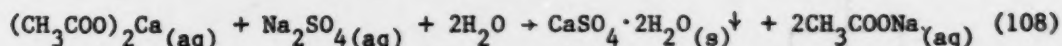
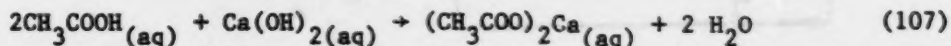
The liquid effluent flows to the combination absorber holding tank and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production reactor while the flue gas enters an acetic acid recovery section. This recovery section has been added because as the scrubbing solution passes through the $\text{SO}_2\text{-NO}_x$ absorber, some of the acetic acid is vaporized. Thus to prevent the excessive loss of acetic acid from the system, the exiting flue gas is passed countercurrently to an aqueous NH_3 solution in the final stage of the absorption section. The acetic acid is reabsorbed and undergoes the following reaction.



The flue gas is then passed through a mist eliminator, reheated, and sent to the stack.

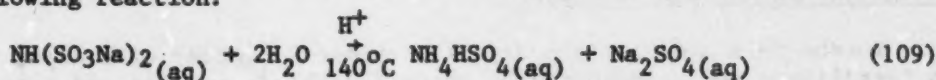
The liquid effluent from the acetic acid recovery section drops into a holding tank from which most of the scrubbing solution is recycled after makeup aqueous NH_3 has been added. The remaining portion is pumped to the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production reactor for further processing.

In the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production reactor the absorbent is mixed with both the purge from the acetic acid recovery section and a fresh limestone slurry stream. The following reactions occur in the resulting mixture.



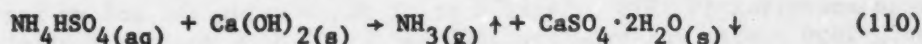
Most of the liquid from the combination $\text{SO}_2\text{-NO}_x$ absorber holding tank- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production reactor is recirculated through the absorber after makeup acetic acid and catalyst have been added. A small purge stream from this holding tank-reactor is removed and divided into two streams. The smaller stream is sent to the NH_3 reactor while the remainder is pumped to a centrifuge where the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals are removed as a byproduct stream. The centrate from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ centrifuge is split into two streams: one

is recycled to the $\text{SO}_2\text{-NO}_x$ absorber and the other is pumped to a hydrolysis reactor in the $\text{NH}(\text{SO}_3\text{Na})_2$ decomposition section. Makeup H_2SO_4 is added to this mixing reactor and the $\text{NH}(\text{SO}_3\text{Na})_2$ is hydrolyzed to NH_4HSO_4 and Na_2SO_4 by the following reaction.

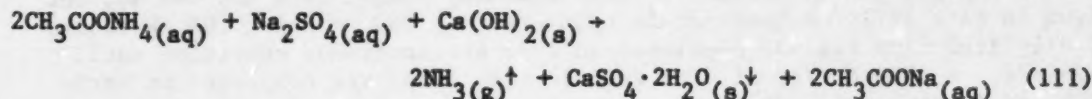


The effluent from this hydrolysis reactor is recycled to the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production reactor.

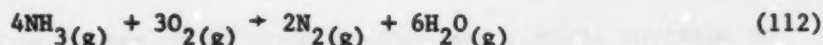
In the NH_3 reactor the small purge stream from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production reactor is mixed with a makeup lime slurry to neutralize the solution and yield the following reaction.



Any remaining ammonium acetate in this purge stream also reacts with the lime slurry to yield NH_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and sodium acetate:



The liquid effluent from the NH_3 -stripping unit is recycled to the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production reactor. The NH_3 off-gas from these reactions is stripped from the solution by an injected air stream and sent to a catalytic reactor where the NH_3 is oxidized at $350\text{-}400^\circ\text{C}$ ($660\text{-}750^\circ\text{F}$) to form molecular N_2 by the following reaction.



The off-gas, containing primarily molecular N_2 and H_2O , from this reactor is recycled through the deacetating section of the absorber.

Status of Development

The Kureha simultaneous $\text{SO}_2\text{-NO}_x$ removal system was developed as a simple modification of their original sodium acetate- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ FGD process. Initial bench-scale tests, treating $250 \text{ Nm}^3/\text{hr}$ (0.08 MW equiv), were begun in 1973. The simultaneous $\text{SO}_2\text{-NO}_x$ removal process was scaled up and operations begun in early 1976 in a $5000 \text{ Nm}^3/\text{hr}$ (1.6 MW equiv) pilot plant at Kureha's Nishiki plant. The heavy oil-fired flue gas typically contained 1100-1700 ppm SO_2 , 160-240 ppm NO_x , 2-4% O_2 , and 0.15 g/ Nm^3 of dust. During a 3000-hr (120-day) continuous test, the system was able to demonstrate more than 99% SO_2 removal and 80-90% NO_x removal with negligible acetic acid emissions. Future plans for this system have not been made available.

The Kureha system has not been tested on flue gas from a coal-fired boiler.

The next development step for this process would apparently be the testing of a prototype unit in the 5-50-MW range. Also, this process's ability to treat flue gas from a coal-fired boiler needs to be demonstrated.

Background of Process Developer

Kureha is a medium-sized Japanese chemical company with major interest in fertilizers and petrochemicals as well as basic organic and inorganic chemicals. Kureha entered the air pollution control field in 1967 with the initial bench-scale testing of their Na_2SO_3 FGD system. After additional pilot-plant work during 1968, several commercial plants based on this Na_2SO_3 FGD technology were completed during the early 1970's. This original Na process was later modified in 1971 to incorporate acetic acid and the new system was renamed the sodium acetate- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ process. A bench-scale unit (0.03 MW equiv) to demonstrate this improved FGD process was built and began operating in 1973. Later a pilot plant using the sodium acetate- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ system and treating 5000 Nm^3/hr (1.6 MW equiv) of oil-fired flue gas began operating in March 1975.

Initial investigation into the possibility of modifying the sodium acetate- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ FGD system to simultaneously remove both SO_2 and NO_x was begun in late 1971. A bench-scale unit treating 250 Nm^3/hr (0.08 MW equiv) of oil-fired flue gas was completed in 1973 and continued operation until mid-1974. A 5000 Nm^3/hr (1.6 MW equiv) pilot plant was completed in early 1976 and is still operating.

Also, Kureha has recently begun the development of a dry SCR process using NH_3 . The initial research was finished in 1975 and a bench-scale unit (0.1 MW equiv) began operating in early 1976. Scaleup to a pilot plant (1.6 MW equiv) was completed in late 1976 and testing was scheduled to begin in February 1977.

No American company has been licensed by Kureha to market this technology in the U.S. However, Kureha has recently established a liaison office in New York City through which inquiries about this process are handled.

Published Economic Data

The total capital investment and annual revenue requirements for the Kureha wet reduction process have been estimated (75) as 9820 Myen and 4460 Myen/yr respectively. These estimates are based on treating flue gas from a 500-MW oil-fired boiler containing 1500 ppm SO_2 , 200 ppm NO_x , and 4% O_2 with a Japanese construction site and March 1977 costs. Assuming 300 yen/\$ these costs would be equivalent to approximately \$65/kW for capital investment and 4.8 mills/kWh for the revenue requirements.

Raw Material, Energy, and Operation Requirements

The following raw material, utility, and operation requirements are preliminary estimates by Kureha and are based on a 500-MW oil-fired boiler treating flue gas containing 1500 ppm SO_2 , 200 ppm NO_x , and 4% O_2 (dry basis). The SO_2

and NO_x removal efficiencies were 99 and 87% respectively. Under these conditions the raw material requirements would be: (All quantities in tons are assumed to be metric tons.)

Raw material	Quantity, kg/hr
$\text{Ca}(\text{OH})_2$	9,700
H_2SO_4	3,900
Catalyst	100
Acetic acid	60
NaOH	60

The utility requirements would be:

Utility	Quantity
Electricity	9,000 kW
Steam	14 tons/hr
H_2O	66 tons/hr
Fuel oil	5.5 kl/hr

The only major byproduct under these assumptions would be 22.5 tons/hr of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The number of operators for the system would be two men per shift. The maintenance requirements have not been made available.

Technical Considerations

Although the Kureha process does not appear to be as complex as the other wet, absorption-reduction processes, it is still much more complex than the dry, NO_x removal processes. The process control requirements will be similar to most of the other wet reduction processes with the major problem being the large equipment requirements.

The NO_x removal efficiency for the Kureha process will be sensitive to both the O_2 and the SO_2 concentration in the flue gas for the same reason as the other wet, absorption-reduction processes. The catalyst for this process is a Fe^{+2} chelating compound which forms a complex with the relatively insoluble NO to aid the absorption process. As the O_2 concentration in the flue gas increases, more of the Fe^{+2} ion is oxidized to the Fe^{+3} ion by flue gas O_2 absorbed into the solution, and hence less of the chelating compound in the Fe^{+2} form would be available to aid in the absorption of NO . In addition, the SO_2 in the flue gas, when it is absorbed in the scrubbing solution, is used to reduce the absorbed NO_x . Thus, when the SO_2 levels are low or the O_2 levels in the flue gas are high, a larger proportion of the SO_3^- ion is consumed by oxidation and less is available to reduce the absorbed NO_x . The SO_2 removal efficiency, on the other hand, would be relatively insensitive to the flue gas concentration.

The packed-bed towers used to absorb the NO, even with the use of the catalyst, will be much larger than the absorber required for their sodium acetate-CaSO₄·2H₂O FGD system since the absorption mechanism for removing the NO is similar to that in the other wet, absorption-reduction process. The operating parameters for the SO₂-NO_x absorber are an L/G of 20-30 1/Nm³ (125-185 gal/kaft³ at 127°F) and a superficial gas velocity in the range of 1-3 m/sec (3.3-10 ft/sec). The deacetating section of the absorber, which contains perforated plates, operates at an L/G ratio of approximately 2.0 1/Nm³ (12.5 gal/kaft³ at 127°F).

The extreme differences in solubilities of SO₂ and NO leads to the unusual situation where the SO₂ is rapidly stripped from the flue gas in the lower portion of the absorber while the NO is gradually absorbed over the entire length of the absorber. This large difference in solubility is indirectly the primary reason for the excellent SO₂ removal efficiency and the insensitivity of the SO₂ removal efficiency to flue gas composition. That is, in order to remove the NO, the absorber is oversized for SO₂ removal. This large difference in the solubilities of SO₂ and NO_x also explains why such a relatively high concentration of the catalyst is required. The catalyst is needed to form a complex with the absorbed NO and transport the NO_x to the lower portion of the absorber where there is a higher concentration of the SO₃⁻ ion available to reduce the NO_x.

Retrofitting this system to a conventional coal-fired power plant equipped with a cold ESP should be relatively easy if additional land is available nearby. The land areas would be relatively large to accommodate both the large equipment requirements in the regeneration section and the limestone preparation section. The only modifications to the existing equipment may be the removal of the cold ESP and the installation of a common plenum to feed the two scrubber trains.

The use of a common plenum would give the process a relatively good turndown capability since a combination of the scrubber trains could be shut down completely. The primary consideration during turndown will be flue gas O₂ and SO₂ concentrations. In general when the boiler load is reduced, the air is usually not reduced and hence with the higher O₂ and lower SO₂ levels, the NO_x removal efficiency will decrease. The SO₂ removal efficiency should not be affected during turndown.

Most of the equipment and piping for this process would be elastomer-lined carbon steel to prevent corrosion and erosion problems associated with the circulating solutions. The only exceptions to this lining would be the flue gas ducts which will be constructed of Inconel 625 and the decomposition reactor which will require glass-lined carbon steel.

Environmental Considerations

The SO₂ and NO_x removal efficiencies for the Kureha simultaneous SO₂-NO_x removal system during pilot-plant testing on oil-fired flue gas were approximately 99 and 80%, respectively, but the denitrification efficiency is dependent on the inlet flue gas composition. For good NO_x removal, i.e., 80%, a minimum mol ratio of SO₂:NO_x of about (2.5-3.0):1 is required depending on the

flue gas O_2 concentration. The higher the flue gas O_2 levels the higher the mol ratio of $SO_2:NO_x$ must be for the same NO_x removal.

The SO_2 is absorbed as Na_2SO_3 , oxidized to Na_2SO_4 , converted to $CaSO_4 \cdot 2H_2O$, and removed as a byproduct. The NO_x is absorbed, reduced to complex N-S compounds, and decomposed to form molecular N_2 . Only a trace of NO_3^- is expected to be formed and hence will not present a significant wastewater problem.

The use of an NH_3 solution to scrub the gas exiting from the absorber removes essentially all of the acetic acid vaporized from the absorber scrubbing solution, but the resulting possibility of NH_3 emissions could be considered a secondary source of pollution.

The byproduct $CaSO_4 \cdot 2H_2O$ formed will probably contain too many impurities to be sold in the U.S. and hence, could probably only be used as landfill material.

Critical Data Gaps and Poorly Understood Phenomena

The major data gaps for the Kureha simultaneous SO_2 - NO_x removal process would include the following:

1. Stream compositions
2. Pilot-plant results

Poorly understood phenomena would include primarily the actual reactions involved in this process. Kureha has only listed some of the reactions occurring in each phase of the process and many of these appear to be overall reactions and as such, the basic mechanisms are not clear. This is particularly true in the NO absorption section where the most complex process chemistry is occurring. In addition, the conversion of the deacetating solution from a limestone slurry to an NH_3 solution, with its associated problems, has not been explained.

Advantages and Disadvantages

The advantages and disadvantages for the Kureha sodium acetate- $CaSO_4 \cdot 2H_2O$ simultaneous SO_2 - NO_x removal process are nearly identical with the advantages and disadvantages of the other wet, absorption-reduction processes and are listed below.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Produces a potentially marketable byproduct ($CaSO_4 \cdot 2H_2O$)
4. Is a slight modification of a commercially available FGD system
5. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

1. Requires significant amounts of energy for the regeneration step

2. Has not been tested on coal-fired flue gas
3. Incorporates questionable design features (final-stage NH_3 scrubbing)
4. Uses significant amounts of stainless steel or exotic materials for process equipment
5. Has a low superficial gas velocity in the absorber (< 10 ft/sec)
6. Has a high L/G ratio in the absorber (> 70 gal/kaft³)
7. Requires flue gas reheat for plume buoyancy
8. Requires flue gas constituents within specific ranges for high NO_x removal
9. Requires an expensive liquid-phase catalyst

MITSUBISHI HEAVY INDUSTRIES PROCESS - WET, OXIDATION-ABSORPTION-REDUCTION (NO_x-SO_x)

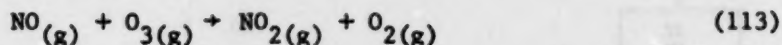
Process Description and Principles of Operation (5, 12, 21, 22)

Mitsubishi Heavy Industries (MHI) has developed a wet, oxidation-absorption-reduction process for the simultaneous removal of SO₂ and NO_x. MHI uses O₃ for the gas-phase oxidation of NO to NO₂, thereby overcoming the problem of the relative insolubility of NO. Once the NO_x is converted to the more soluble NO₂, these oxides are absorbed, reduced by the SO₃²⁻ ion, and recovered as NH₃. The SO₂ is absorbed by the scrubbing solution to form the SO₃²⁻ ion, oxidized to the SO₄²⁻ ion, and removed as a byproduct CaSO₄·2H₂O stream.

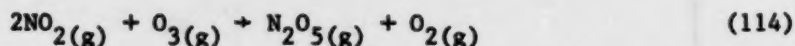
The overall system is composed of five major sections including (1) pre-scrubbing, (2) gas-phase oxidation, (3) absorption of both SO₂ and NO_x, (4) byproduct CaSO₄·2H₂O production, and (5) N-S decomposition. The basic outline for the MHI process is shown in the block flow diagram in Figure 19.

As in each of the other wet-scrubbing processes, the flue gas from the air heater is first passed through a prescrubber which removes about 90% of the particulates and essentially all of the Cl⁻ from the flue gas, and cools the gas from 150°C (300°F) to 53°C (127°F) by adiabatic humidification. The liquid effluent from the particulate scrubber drops into a holding tank from which most of the liquid is recirculated through the scrubber after makeup H₂O has been added. Although not mentioned by MHI, it is assumed that the remaining liquid in the holding tank is purged to either a centrifuge or holding pond to remove the flyash and thus prevent the buildup of flyash in the scrubbing solution.

After passing through a mist eliminator, the flue gas enters a duct between the prescrubber and the absorber and, before entering the absorber, is injected with a stoichiometric amount of O₃ as a weak (<5%) O₃-air mixture. This O₃-air mixture is generated onsite using a battery of corona discharge units, since O₃ is a strong oxidant and is too unstable to be stored in large quantities. The NO in the flue gas is rapidly and selectively oxidized by O₃ according to the following reaction.



Proper positioning of the O₃-air injection nozzles will eliminate poor mixing of the gases and thus minimize the following undesirable side reaction.



Following O₃ oxidation the flue gas passes cocurrently in a grid-packed tower with a limestone or lime slurry containing a dissolved catalyst.

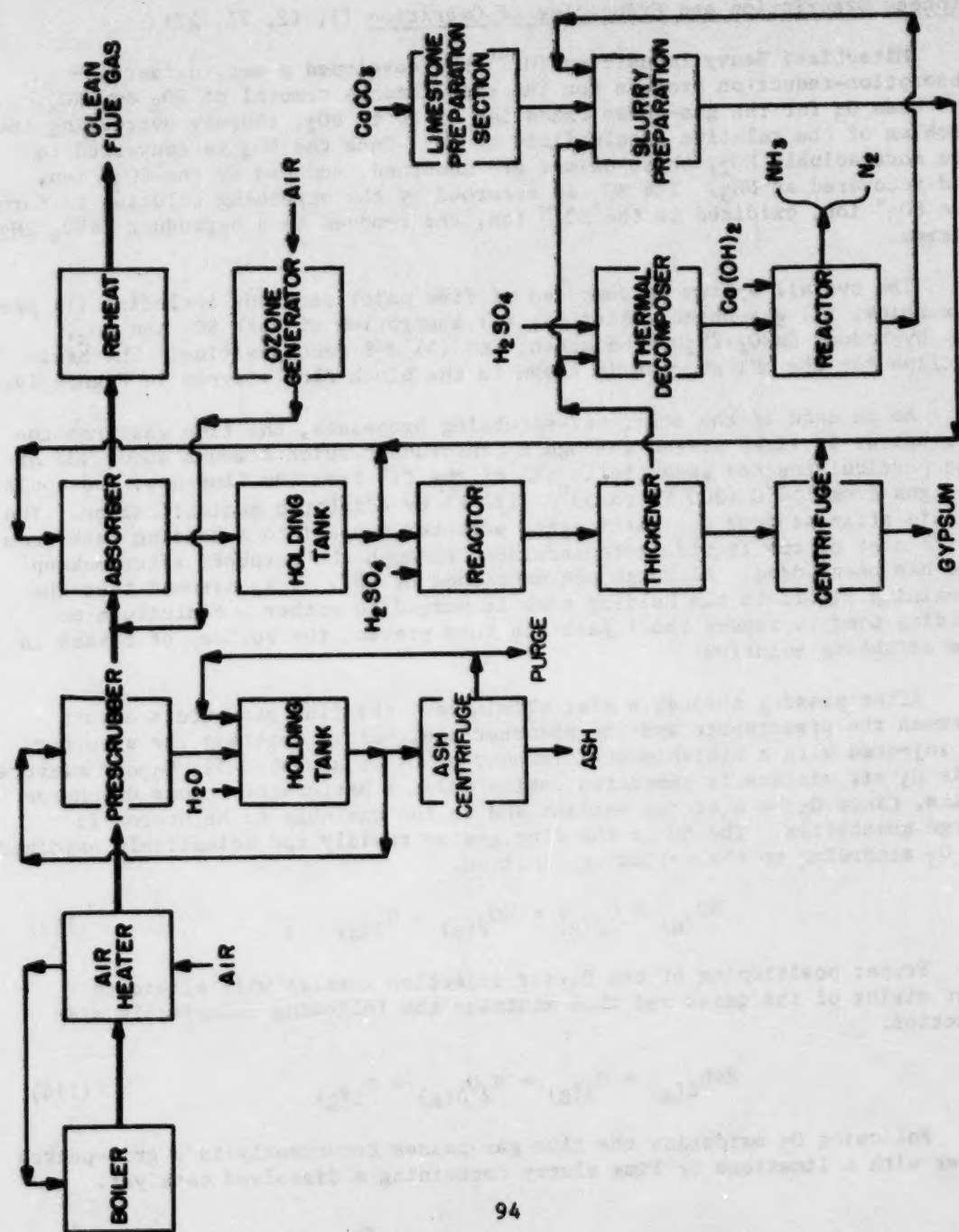
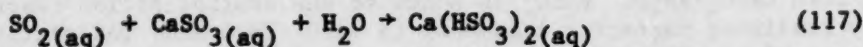
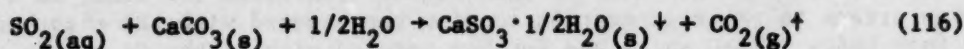
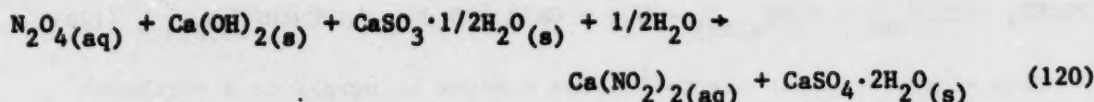


Figure 19. Flow Diagram of Mitsubishi Heavy Industries Wet Process.

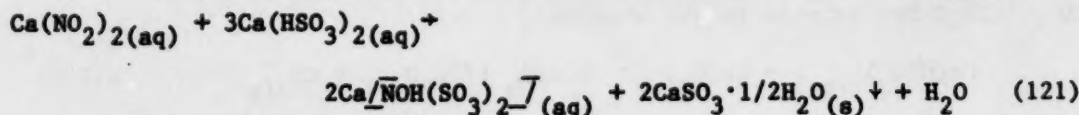
The SO_2 is absorbed from the flue gas and undergoes the following liquid-phase reactions.



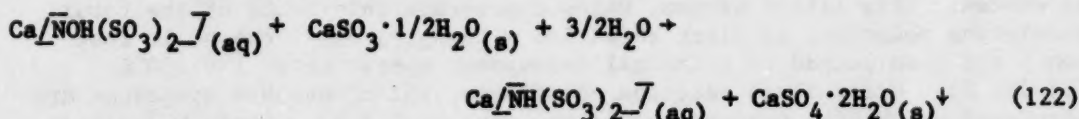
The NO_2 , which is absorbed into the scrubbing solution more slowly than the SO_2 , undergoes the following reactions.



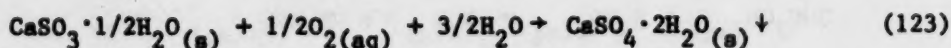
Once both the SO_2 and NO_2 have been absorbed, the NO_2^- formed by reaction (120) are reduced by the HSO_3^- ion formed in reaction (117) to form complex N-S compounds, such as hydroxylamine $[\text{NOH}(\text{SO}_3)_2]^-$ salts.



These complex N-S compounds are further reduced by the $\text{SO}_3^{=}$ ion in the scrubbing solution to produce $\text{NH}(\text{SO}_3)_2^{=}$ salts by the following reaction.

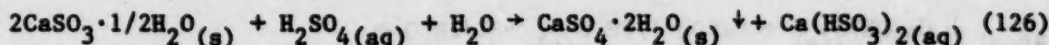
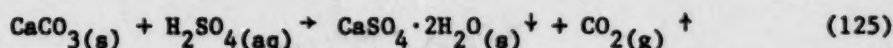
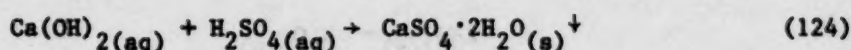


In addition to these primary reactions, an important secondary reaction occurs in the absorber. Some of the $\text{SO}_3^{=}$ ions formed in the scrubbing solution are oxidized to the $\text{SO}_4^{=}$ ion by O_2 absorbed from the flue gas, i.e.,

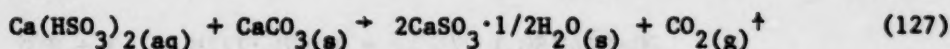


The flue gas from the absorber, after passing through a mist eliminator, is reheated for plume buoyancy and sent to the stack.

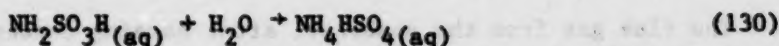
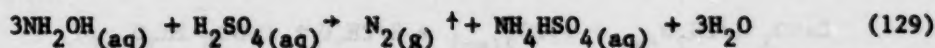
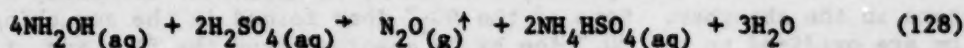
The effluent slurry from the absorber, containing a mixture of dissolved N-S compounds and insoluble $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, drops into an absorber holding tank. A small purge stream (10-20%) of the circulating solution is removed from this holding tank and pumped to a neutralization reactor in the regeneration section while the remaining effluent from this holding tank is recirculated through the absorber after makeup limestone slurry has been added. Much of the original limestone (or lime) in this purge stream to the regeneration section has reacted with the absorbed SO_2 to form $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ which has further reacted with either O_2 or the NO_x to form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. H_2SO_4 is added to the neutralization reactor to convert any remaining unreacted limestone to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and, indirectly, to convert any insoluble $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ to soluble calcium bisulfite $[\text{Ca}(\text{HSO}_3)_2]$ and insoluble $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. These primary reactions occurring in the neutralization reactor include:



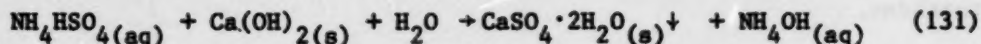
This slurry from the neutralization reactor is pumped to a thickener from which the bottoms, containing mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are pumped to a centrifuge where the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals are separated as a byproduct stream. The mother liquor from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ centrifuge is sent to the limestone slurry preparation tank. As makeup limestone is added to this bisulfite $[\text{Ca}(\text{HSO}_3)_2]$ rich liquor, the $\text{Ca}(\text{HSO}_3)_2$ will be converted back into $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ for recycle to the absorber.



The thickener overflow, containing the H_2O soluble N-S compounds, is split into two streams: one for recycle to the limestone slurry preparation tank and the other for further processing to remove these N-S compounds from the system. This latter stream, which represents only 5-10% of the total circulating solution, is first acidified with H_2SO_4 until the pH is less than 1 and then pumped to a thermal decomposer operating at $130-150^\circ\text{C}$ ($265-300^\circ\text{F}$). Under these reaction conditions, 95% of the N-S compounds are hydrolyzed to NH_4HSO_4 during a residence time of 1-2 hr. These hydrolysis reactions include:



The NH_4HSO_4 solution from the decomposer is pumped to a neutralization reactor where this solution is mixed with a slaked lime slurry to yield ammonium hydroxide (NH_4OH) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.



MHI has suggested three possible methods of treating this resulting slurry to remove the NH_4OH from the system. These three hypothesized options are:

1. Increase the pH of the slurry until the NH_4OH decomposes into NH_3 and then separate the gaseous NH_3 (10-15% by vol) from the N_2 and N_2O gas stream by an unspecified process.
2. Use high temperature to thermally decompose this NH_3 to molecular N_2 .
3. Reclaim the NH_4OH in a stripping unit with makeup H_2O .

Once the NH_4OH has been removed, the remaining $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ slurry is recycled to the limestone slurry preparation tank.

Status of Development

Initial work on the MHI process for the simultaneous removal of SO_2 and NO_x was begun on a bench-scale unit in June 1974. This unit treated $200 \text{ Nm}^3/\text{hr}$ (0.06 MW equiv) of flue gas from a heavy oil-fired boiler until December 1975. Scaleup to a pilot plant treating $2000 \text{ Nm}^3/\text{hr}$ (0.6 MW equiv) of flue gas from a heavy oil-fired boiler was completed in June 1975. During two separate continuous month-long tests on this flue gas containing 800-1100 SO_2 , 180-220 ppm NO_x , 3-8% O_2 , and 0.09-0.12 g/ Nm^3 of dust, the MHI process was able to maintain 95% SO_2 removal and 80-90% NO_x removal. This process has not been tested on flue gas from a coal-fired boiler.

At the present time plans are being formulated to construct a prototype or commercial unit (33-67 MW equiv) but both the type of flue gas to be treated and the site of the plant have not been specified.

Background of Process Developer

MHI has been involved in the development of air pollution technology since the completion of their first FGD system in 1972. Since then MHI has completed approximately 50 desulfurization units with a total capacity of almost 20 million Nm^3/hr (6700 MW equiv).

The MHI wet simultaneous SO_2 - NO_x removal process, which has been under development since 1974, is very similar to their commercial FGD system with the only major modifications being the addition of an O_3 generation section and an NH_3 recovery section.

No American company has been licensed by MHI to market their process in the U.S., but MHI does have a liaison office in New York City, through which inquiries about this process are handled.

Published Economic Data

No estimates for either the total capital investment or the annual revenue requirements for the MHI simultaneous SO_2 - NO_x process have been published. The costs, however, for this process will probably be on the same order of magnitude as the other Ca-based oxidation-absorption-reduction processes.

Raw Materials, Energy, and Operation Requirements

The major raw materials required for the MHI process are limestone, slaked lime, H_2SO_4 , and O_3 . Limestone and H_2SO_4 are common industrial raw materials and readily available. The O_3 , however, due to its extreme reactivity will be generated onsite by corona discharge and hence is not a raw material but an energy requirement.

The raw material requirements listed below were estimated by MHI for a system treating $100,000 \text{ Nm}^3/\text{hr}$ (33 MW equiv) of flue gas from an oil-fired boiler containing 1,500 ppm SO_2 and 150 ppm NO_x . The SO_2 and NO_x removal efficiencies were assumed to be 95 and 90% respectively. (All quantities measured in tons are assumed to be metric tons.)

<u>Material</u>	<u>Quantity</u>
Limestone	0.58 ton/hr
Slaked lime	0.05 ton/hr
H_2SO_4	0.08 ton/hr
Catalyst	<0.8 kg/hr

The energy requirements for treating $100,000 \text{ Nm}^3/\text{hr}$ under the same basis as above are:

<u>Utility</u>	<u>Quantity</u>
Electricity	1750 kW
Industrial water	12.5 tons/hr
Steam	5.0 tons/hr

The operating manpower and maintenance requirements for this process have not been published.

Technical Considerations

The MHI simultaneous SO_2 - NO_x process, using O_3 for the gas-phase oxidation of NO and a $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ scrubbing solution to absorb the resulting NO_2 , appears to require about the same amount and type of process equipment as the other oxidation-absorption-reduction processes. As a result the process control requirements for this process will be very similar to that required for the other wet simultaneous FGD and denitrification systems of this type. The major process control problem will be the O_3 generation and injection system since the O_3 , once generated, is extremely reactive and cannot be stored economically. If the O_3 is injected in less than

stoichiometric amounts, the NO_x removal efficiency will decrease, and if it is injected in more than stoichiometric amounts, the revenue requirements for this system would rapidly increase since the cost of O_3 is a major constituent in the annual revenue requirements of this system.

The SO_2 removal efficiency is insensitive to the inlet flue gas composition since there are no interfering gas species and the absorber is essentially an oversized FGD scrubber. With the higher L/G ratio in the absorber required for denitrification, the SO_2 removal efficiency in this process is expected to consistently remain above 90%.

The NO_2 removal efficiency for this process is relatively insensitive to the inlet flue gas composition provided that the mol ratio of $\text{SO}_2:\text{NO}_2$ in the flue gas is >2.5 . For most coal-fired boilers, the flue gas would be expected to meet this requirement with the only possible exception being flue gas from boilers fired with low-S western coal. This relatively high mol ratio is necessary since the absorbed SO_2 , the SO_3^- ion, is needed to reduce the absorbed NO_x .

The absorber selected by MHI is a grid-packed tower in which the $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ slurry and the flue gas are passed cocurrently with each other. Although the actual operating conditions in this absorber have not been published, the absorber parameters are assumed to be similar to those in a conventional limestone FGD system. The L/G ratio in the absorber would probably be in the range of 7-10 l/Nm^3 (44-62 gal/kuft³ at 127°F) or slightly higher than a conventional limestone FGD system to accommodate the increased difficulty in absorbing NO_x . In addition, a proprietary H_2O soluble catalyst has been introduced into the scrubbing solution to aid in the absorption of the NO_x .

Although this process has not been tested on flue gas from a coal-fired boiler, MHI does not expect any serious technical problems in converting this system to coal-fired flue gas providing that a prescrubber is inserted to remove the particulates and Cl^- . The economics of operating this system, however, will be drastically altered in that approximately three times as much O_3 will be required to oxidize the increased NO_x levels in the coal-fired flue gas. In addition, the electrical energy consumed to generate the O_3 will also increase sharply. In fact, in a previous study (49) the O_3 consumption alone is expected to require 9-10% of the generating capacity of the boiler when the inlet NO_x concentration is 600 ppm. Thus this process, as with the other oxidation-absorption-reduction processes, would be very expensive unless combined with some type of boiler modification system to reduce NO_x levels below 600 ppm before reaching the wet-scrubbing system.

As is common for the wet simultaneous removal processes, retrofitting this system on existing power plants would be relatively easy if sufficient land is available nearby for siting the various process equipment. The major modification to the existing plant would be the installation of a common plenum from the boilers or the ESP to feed the four scrubber trains on a 500-MW boiler. The existing cold ESP would be removed and replaced with the venturi-type prescrubbers to remove the Cl^- as well as the flyash

from the flue gas. The use of a common plenum and four absorber trains will allow this system to cycle with the boiler by simply closing off any combination of trains. The O₃ generation section can also be easily turned down since this section is made up of a battery of small O₃ generators, any combination of which can be shut down independently.

Most of the process equipment and piping for this process will need to be elastomer-lined carbon steel to prevent the corrosion and erosion problems associated with handling circulating limestone slurries and Cl⁻ solutions. Exceptions to this elastomer lining include the flue gas ducts, the thermal decomposer, and the neutralizing reactor. The flue gas ducts will be constructed of Inconel 625 to prevent both H₂SO₄ mist corrosion and the oxidation associated with the use of O₃. The decomposer will require either stainless or glass-lined steel due to the high temperature and acidity required to hydrolyze the N-S compounds. The neutralizing reactor will require stainless steel to prevent corrosion by the NH₃ atmosphere generated in this reactor.

Environmental Considerations

During the initial 8 mo of operation in a small pilot-plant unit treating 2000 Nm³/hr (0.6 MW equiv) of flue gas containing 1500 ppm SO₂, 150 ppm NO_x, 4.5% O₂, and 0.1 g/Nm³ (0.04 gr/sft³ at 32°F) of dust, the MHI process was able to maintain 90% NO_x removal and better than 95% SO₂ removal. The SO₂ is absorbed, oxidized, and recovered as byproduct CaSO₄·2H₂O while the NO_x is absorbed, reduced, and recovered as a weak (10-15%) NH₃ gas stream. At the present time MHI has not selected a method of removing this NH₃.

The NO_x removal efficiency is, of course, dependent on the amount of O₃ injected. If the amount of O₃ injected decreases below the stoichiometric requirement, the NO_x removal will drop below 90%. A complete failure of the O₃ generation section will result in only approximately 5% of the NO_x being removed. On the other hand a complete failure of the O₃ generation section will not affect the SO₂ removal efficiency and it will remain above 95%.

The O₃ used to oxidize the NO in the flue gas is a very strong oxidizing agent and even at low concentrations presents a significant work hazard for this process.

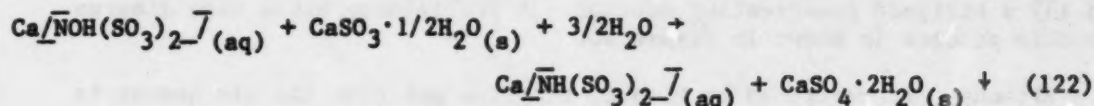
Critical Data Gaps and Poorly Understood Phenomena

Included are critical data gaps and the preliminary engineering assumptions used to fill in these critical data gaps.

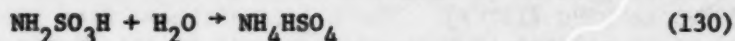
1. The L/G ratio and superficial gas velocity in the absorber (assumed to be 44-62 gal/kaft³ and 3-10 m/sec respectively)
2. The conversion of SO₃⁻ to SO₄⁻ in scrubber solution with flue gas having 4% O₂
3. The catalyst used for NO_x reduction

4. The operating conditions in the process equipment and stream compositions
5. Maintenance and manpower requirements
6. Estimated total capital investment and annual revenue requirements

Included under poorly understood phenomena would be the sequence of reactions involved in reducing the NO_2^- salts to complex N-S compounds. The series of reactions given by MHI [see reactions (121), (122), (128), (129), and (130)] include apparent inconsistencies. For example, from other processes calcium sulfamine $[\text{CaNH}(\text{SO}_3)_2]$ formed by reaction (122) given below



would more likely be calcium sulfamate $[\text{Ca}(\text{NH}_2\text{SO}_3)_2]$, particularly since one of the hydrolysis reactions given is the hydrolysis of the NH_2SO_3^- ion, i.e.,



Although not mentioned by the process developer, it is assumed that at least some NO_3^- salts would be formed when the NO_x is absorbed. If sufficient wastewater NO_3^- is formed the disposal of these salts could be a problem.

Advantages and Disadvantages

As with the other wet simultaneous SO_2 - NO_x removal processes using gas-phase oxidation, this process has certain advantages and disadvantages over dry NO_x processes and wet nonoxidation processes. These advantages and disadvantages are listed below.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Produces a potentially marketable byproduct ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
4. Is a slight modification of a commercially available FGD system
5. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

1. Forms secondary source of pollution (15% NH_3 off-gas)
2. Requires significant amounts of energy for the regeneration step
3. Has not been tested on coal-fired flue gas
4. Has not been operated for a long-term continuous period
5. Uses significant amounts of stainless steel or exotic materials for process equipment
6. Requires flue gas reheat for plume buoyancy
7. Requires flue gas constituents within specific ranges for high NO_x removal
8. Requires an expensive gas-phase oxidant

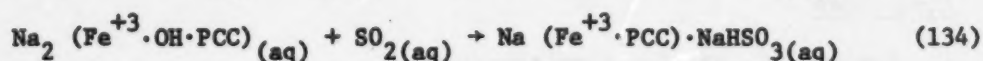
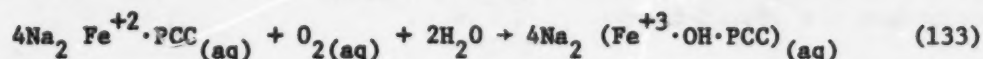
MITSUI ENGINEERING AND SHIPBUILDING PROCESS - WET, ABSORPTION-REDUCTION (NO_x-SO_x)

Process Description and Principles of Operation (3, 5, 16)

This process is in the early stages of development by Mitsui Engineering and Shipbuilding Company, Ltd., and very little information is available as yet. It is a wet, absorption-reduction process which uses an Fe⁺² chelate solution to simultaneously absorb the SO₂ and the NO_x from the flue gas. The SO₂ is absorbed and regenerated to form a concentrated SO₂ gas stream. The NO_x is similarly absorbed, regenerated, and reduced to molecular N₂. The Mitsui wet process consists of five parts including (1) prescrubbing, (2) an NO_x-SO₂ absorption section, (3) a reduction section, (4) a stripping section, and (5) a stripped gas-treating section. A preliminary block flow diagram for this process is shown in Figure 20.

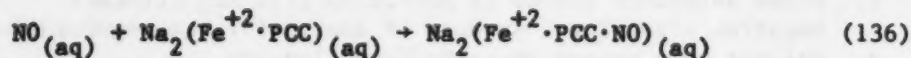
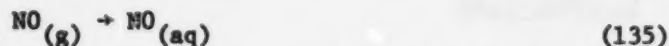
Although not mentioned by Mitsui, the flue gas from the air heater is assumed to pass through a closed-loop prescrubber section before entering the absorber to remove the increased amounts of particulates and Cl⁻ associated with coal combustion. In addition, some of the circulating solution is evaporated to adiabatically humidify and cool the flue gas from 150°C (300°F) to 53°C (127°F). The liquid effluent from the particulate scrubber drops to a holding tank from which most of the liquid is recirculated to the prescrubber after fresh makeup H₂O has been added. A small purge stream is removed from the holding tank, neutralized, and pumped to a disposal pond.

The flue gas from the prescrubber is passed countercurrently to a proprietary Fe⁺² chelate scrubbing solution. As the flue gas passes through the lower portion of the absorber, the SO₂ is rapidly absorbed into the solution and undergoes the following reactions with the oxidized Fe⁺² chelate:



where PCC represents the proprietary chelating compound.

The NO_x, mainly in the form of NO, is gradually absorbed over the entire absorber and is hypothesized to react according to the following reactions:



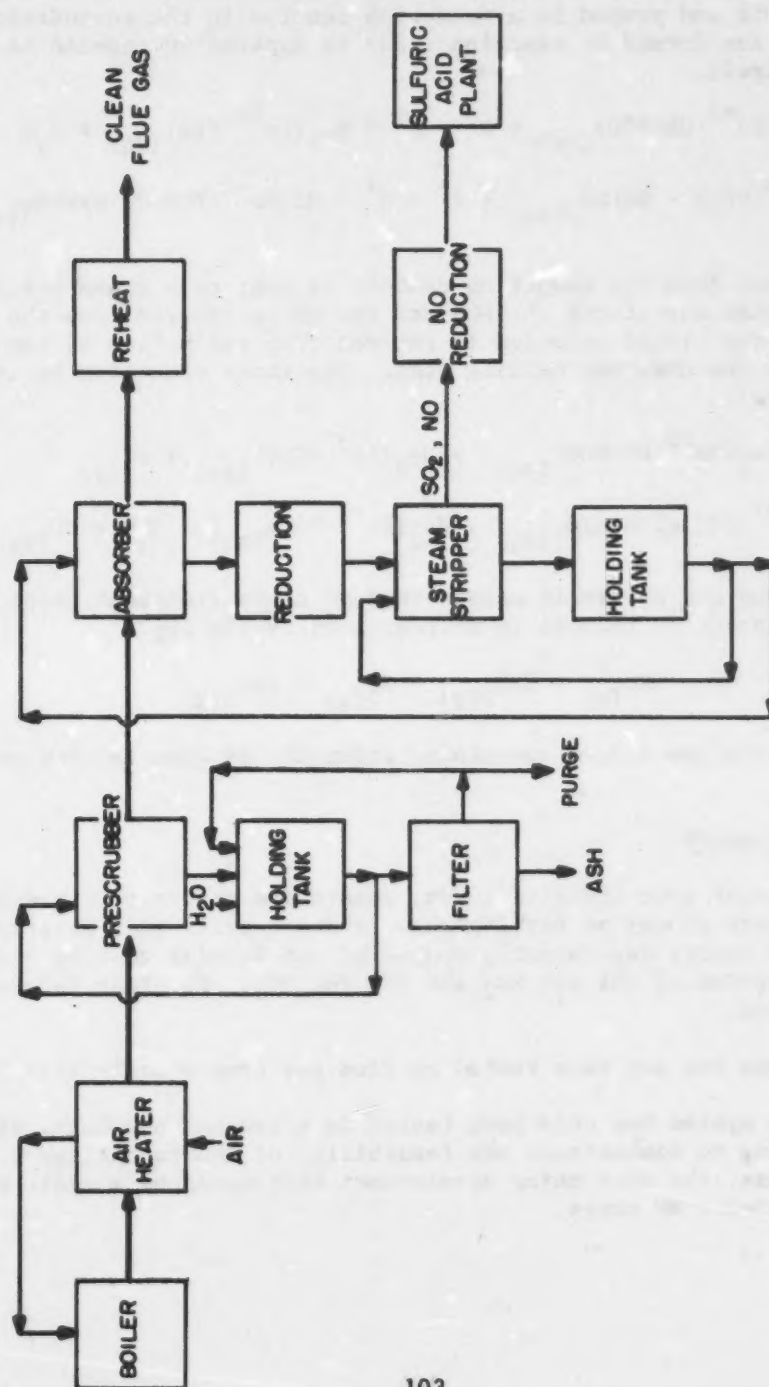
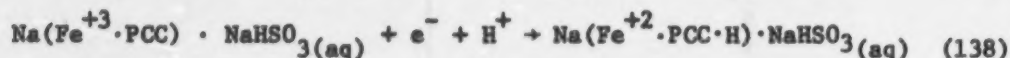
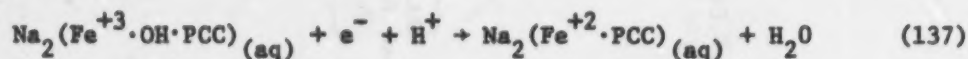


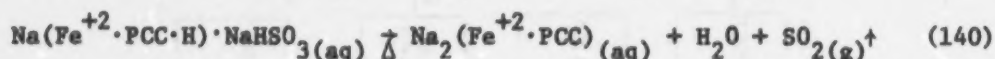
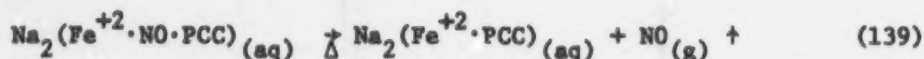
Figure 20. Flow Diagram of Mitsui Engineering and Shipbuilding Co. Wet Process

The flue gas from the absorber is passed through a mist eliminator, reheated, and exited through the stack.

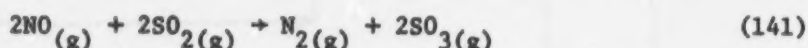
The liquid effluent from the absorber drops to a holding tank from which most of the solution is recirculated through the absorber. A small purge stream is removed and pumped to a reduction reactor in the regenerator section where the Fe^{+3} ion formed by reaction (133) is apparently reduced to the Fe^{+2} ion by electrolysis.



The effluent from the reduction reactor is sent to a steam stripper where an overhead stream containing the SO_2 and the NO is removed from the scrubbing solution while the liquid solution is removed from the bottom of the stripper and recycled to the absorber holding tank. Reactions occurring in the steam stripper include:



The overhead gas stream is passed through a gas treatment section where the NO is catalytically reduced to molecular N_2 by the SO_2 .



The remaining gas stream containing primarily SO_2 can be used to produce H_2SO_4 .

Status of Development

At the present time the Mitsui wet, absorption-reduction process is only in the preliminary stages of development. A bench-scale unit treating 150 Nm^3/hr (0.05 MW equiv) was recently completed and initial testing indicates removal efficiencies of 95% for SO_2 and 85% for NO_x . No other information has been released.

This process has not been tested on flue gas from a coal-fired boiler.

Since this system has only been tested in a bench-scale unit, after extensive testing to demonstrate the feasibility of the technology of this reduction process, the next major development step would be a small pilot plant in the 0.5-2.0 MW range.

Background of Process Developer

Mitsui is a relatively large and diversified Japanese corporation which entered the air pollution control field in the early 1970's. In addition to the development of their lime slurry FGD system, their early involvement in air pollution control included a licensing agreement to build the Dowa aluminum sulfate $[\text{Al}_2(\text{SO}_4)_3]$ - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ FGD system.

In response to the adoption of stringent NO_x emission controls in Japan, Mitsui initially began the development of their dry SCR process using NH_3 . This dry SCR process has reached the commercial stage of development. Recently Mitsui began the development of this wet, absorption-reduction process in addition to their original dry SCR process.

No American company has been licensed by Mitsui to market this process in the U.S. However, Mitsui has a liaison office in New York City through which inquiries about this process are handled.

Published Economic Data

No information on the economics of this process has been published.

Raw Material, Energy, and Operation Requirements

Essentially no information has been published for raw material, energy, and operating requirements.

Technical Considerations

Since little information is available, only very general statements can be made about this process. For instance, it is a wet, absorption-reduction process using an Fe^{+2} chelating compound in the scrubbing solution to absorb NO . Many of the operating parameters and technical considerations in the absorption section will be similar to those specified in the other absorption-reduction processes. The regeneration section, however, is completely different and hence no technical evaluation can be made now with the limited amount of information available.

Environmental Considerations

Essentially no information is available to make any comments on the potential environmental effects of this process.

Critical Data Gaps and Poorly Understood Phenomena

Due to the lack of even general information concerning this process, only the major data gaps will be listed.

1. Operating conditions in the process equipment
2. Stream flows and their composition

3. Nature and description of the regeneration and byproduct treatment section
4. Raw material, energy, and operating conditions
5. Economic data
6. Pilot-plant results

Advantages and Disadvantages

Although other advantages and disadvantages may become apparent after additional data are released, the following list has been completed with the information presently available.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Produces a potentially marketable byproduct (concentrated SO_2 gas)
4. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

1. Requires significant amounts of energy for the regeneration step
2. Has not been tested on coal-fired flue gas
3. Has been tested only in a bench-scale unit
4. Has not been operated as an integrated process
5. Has not been operated for a long-term continuous period
6. Has a low superficial gas velocity in the absorber (<10 ft/sec)
7. Has a high L/G ratio in the absorber (>70 gal/kaft³)
8. Requires flue gas reheat for plume buoyancy
9. Requires an expensive liquid-phase catalyst

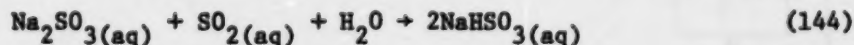
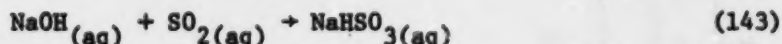
MON ALKALI PERMANGANATE PROCESS - WET, ABSORPTION-OXIDATION (NO_x-SO_x)

Process Description and Principles of Operation (5)

The MON Alkali Permanganate process was jointly developed by Mitsubishi Metal Company, Mitsubishi Chemical Machinery (Mitsubishi Kakoki Kaisha), and Nippon Chemical Industrial Company. As is common with absorption-oxidation processes, the desulfurization step takes place in a separate absorber before the flue gas denitrification step and hence this process is not a simultaneous SO₂-NO_x process. The Mon Alkali system uses a sodium hydroxide (NaOH) scrubbing solution to remove the SO₂ in the FGD absorber and a potassium hydroxide-based (KOH) scrubbing solution containing potassium permanganate (KMnO₄) to absorb the NO_x in the second absorber. The overall process consists of six major sections (1) prescrubbing, (2) SO₂ absorption, (3) oxidation to SO₄²⁻ and formation of Na₂SO₄ in the FGD system, (4) NO_x absorption, (5) NO_x oxidation with permanganate (MnO₄⁻), and (6) removal and regeneration of the MnO₄⁻ oxidant in the denitrification section. The basic outline of this process is shown in a block flow diagram in Figure 21.

Although not specifically mentioned, the process is expected to require a closed-loop prescrubber section when treating flue gas from a coal-fired boiler to remove the increased particulates and Cl⁻ associated with coal combustion. In addition to removing 90% of the particulates and essentially all of the Cl⁻ from the flue gas, the prescrubber also humidifies and cools the gas from 150°C (300°F) to 53°C (127°F). The liquid effluent from the prescrubber drops into a holding tank from which most of the solution is recirculated through the prescrubber after makeup H₂O has been added. The remaining solution from the holding tank is sent to an ash centrifuge where the flyash is separated. Most of the centrate is recycled to the holding tank but a small purge stream is removed and pumped to a waste disposal pond to prevent the buildup of Cl⁻ in the scrubbing solution.

The flue gas from the prescrubber is sent to a desulfurization scrubber in which the gas passes countercurrently to an Na-based scrubbing solution. The SO₂ is rapidly stripped from the solution and undergoes the following reactions:



In addition to these primary reactions, an important secondary reaction occurs in the absorber. Since the SO₃²⁻ ion is present as the soluble Na salt, it is easily oxidized by flue gas O₂ absorbed into the solution, i.e.

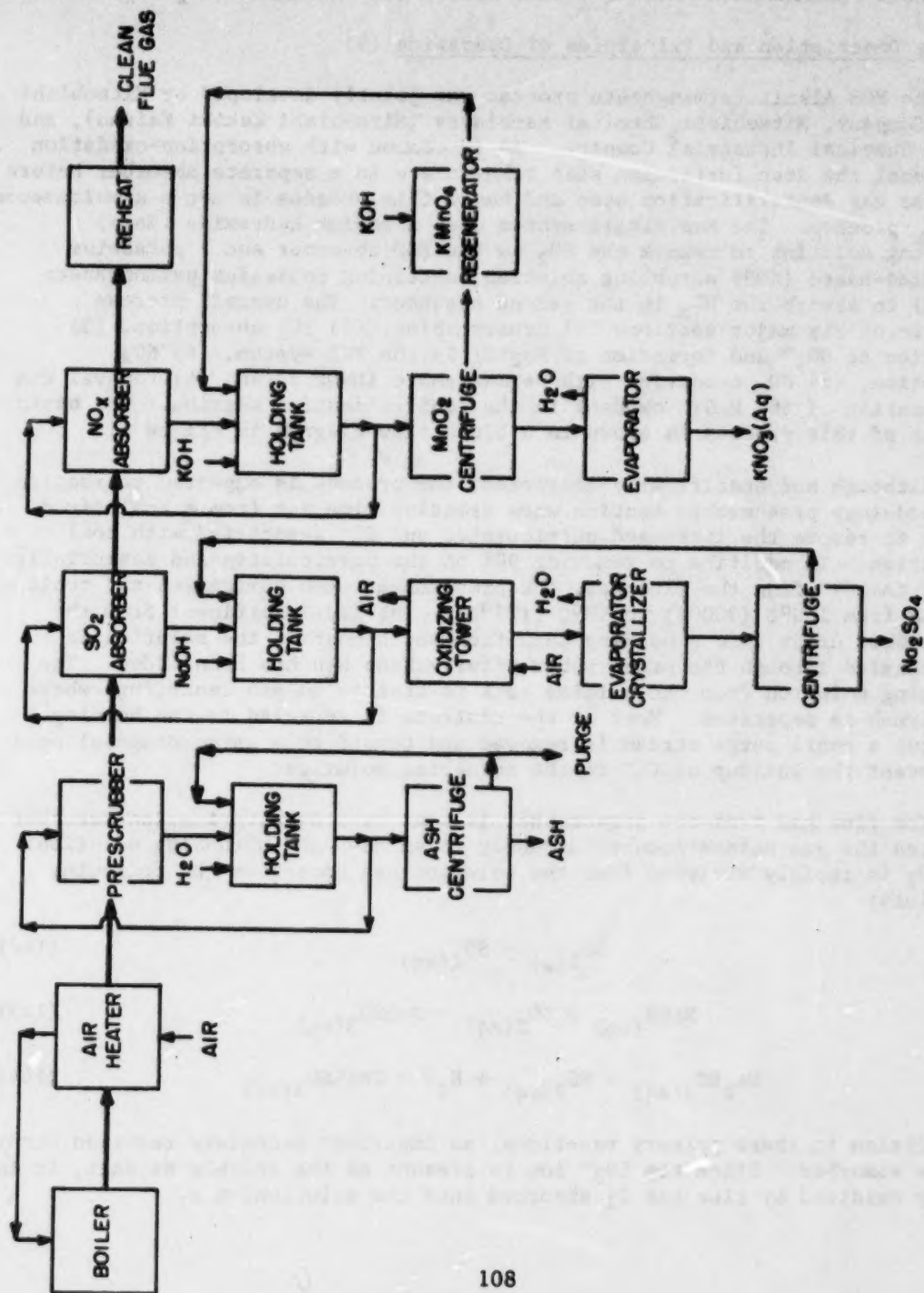
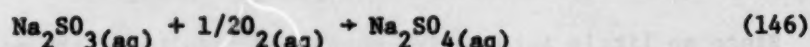


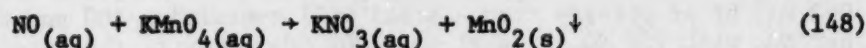
Figure 21. Flow Diagram of MON Alkali Permanganate Process.



The scrubbing solution from the absorber drops into a holding tank from which most of the solution is recycled to the absorber after makeup NaOH has been added. A small purge stream is removed from the holding tank and sent to a regeneration section to remove the absorbed SO_2 as Na_2SO_4 .

Since essentially no information is available on the regeneration system, the following has been assumed. The purged solution is probably pumped to an oxidizing tower to convert the remaining SO_3^{2-} to SO_4^{2-} by reaction (146). Since Na_2SO_4 is very soluble, the effluent from the oxidizer will have to be partially evaporated, cooled in a crystallizer, and centrifuged to remove the byproduct Na_2SO_4 . The mother liquor separated in the centrifuge is recycled to the absorber holding tank.

The flue gas from the FGD section is then passed countercurrently to a KOH solution containing $KMnO_4$ in the second absorber. The NO_x in the flue gas is gradually absorbed over the length of the absorber and once absorbed is readily oxidized by the MnO_4^- ion to form NO_3^- salts. This reaction sequence is hypothesized to be as follows:



The flue gas from the NO_x scrubber is reheated and sent to the stack while the scrubbing solution drops into a holding tank. Most of this solution is recycled to the absorber after makeup KOH and recycle $KMnO_4$ have been added. A small purge stream is removed from the holding tank and sent to the regeneration section where the manganese dioxide (MnO_2) is separated in a centrifuge, converted into MnO_4^- by electrolysis, and recycled to the absorber. The concentrate containing the potassium nitrate (KNO_3) is to be marketed as a liquid fertilizer although it will probably be necessary to concentrate this solution by evaporation before it is sold.

Status of Development

Initial testing of the MON Alkali Permanganate process was begun in late 1972 in a bench-scale unit treating $300 \text{ Nm}^3/\text{hr}$ (0.1 MW equiv) of flue gas from an oil-fired boiler. After approximately 2 yr of testing, a pilot plant treating $4000 \text{ Nm}^3/\text{hr}$ (1.3 MW equiv) was completed. No information has been made available concerning the results of these pilot-plant tests.

This process has not been tested on coal-fired flue gas.

The process developers theorize that the most promising use of this process is for treating off-gases from steel mills rather than power plant

stack gases. The economics of this process for treating flue gas containing large amounts of SO_2 are not competitive when compared with other simultaneous SO_2 - NO_x processes. The high cost of this process under these conditions is primarily due to the excessive consumption of KMnO_4 .

Since so little information about the results of the pilot-plant testing is available, it is difficult to project the next stage of development for this process.

Background of Process Developers

The MON Alkali Permanganate process was developed jointly by Mitsubishi Metal, Mitsubishi KK, and Nippon to convert the NO_x in HNO_3 tail gas to KNO_3 . No information is available on the background of Mitsubishi Metal but Mitsubishi KK is a well-known Japanese manufacturing company. Nippon is a Japanese chemical concern which produces alkali permanganates.

Mitsubishi Metal and Nippon apparently have not had any previous experience in air pollution control. However, Mitsubishi KK has also been involved in the development of a dry NH_3 -based SCR process which is discussed in more detail under the Mitsubishi KK process in the section, Dry NO_x Removal Processes.

Published Economic Data

No information has been published concerning the total capital investment or the annual revenue requirements for treating power plant stack gas using the MON Alkali Permanganate process. However, for treating 200,000 Nm^3/hr of off-gas from a steel mill containing 100 ppm SO_2 and 200 ppm NO_x with 75% NO_x removal and 100% SO_2 removal, the total capital investment has been estimated (113) as \$5 million while the revenue requirements were estimated as \$13-15/k1 of heavy oil. These costs are assumed to be based on a Japanese construction site and mid-1974 dollars.

Raw Material, Energy, and Operation Requirements

No information has been published concerning the raw material, energy, and operation requirements for this process. The major raw material would probably be KOH and NaOH with lesser amounts of makeup limestone and KMnO_4 . The major energy requirements would be fuel oil, for both flue gas reheat and to evaporate the byproduct salt solutions, and electrical energy for both regenerating the KMnO_4 and operating the processing equipment.

Technical Considerations

Since very little information is available on the MON Alkali Permanganate process, a detailed technical assessment of this process is impossible and only general statements can be made.

As in the case of the other wet, absorption-oxidation processes, the use of a liquid-phase oxidant, such as the KMnO_4 used in this process,

brings about two major problems when applied to power plant flue gas.

1. Since SO_2 is also readily oxidized by the liquid-phase oxidant, the SO_2 must be removed in a separate absorber to prevent excessive consumption of the liquid-phase oxidant.
2. The NO_x absorber must be very large to remove the relatively insoluble NO from the flue gas.

Thus, from a technical viewpoint, this process is not a "simultaneous" SO_2 - NO_x removal system but simply a combination of separate desulfurization and denitrification systems.

The NO_x and SO_2 removal efficiency of the MON Alkali Permanganate system should be relatively insensitive to the inlet flue gas composition. The operating costs for this MnO_4^- process, however, will be influenced by the inlet flue gas composition since the amount of KMnO_4 required will be proportional to both the inlet NO_x and SO_2 concentrations.

The byproducts formed in this process, (i.e., Na_2SO_4 and KNO_3) although potentially marketable, will have a difficult time displacing competing natural sources. In particular, KNO_3 as a weak aqueous solution would have very little demand as a liquid fertilizer.

Since this is a wet simultaneous process, retrofitting this system on existing power plants should be relatively easy if sufficient land is available nearby for the siting of the process equipment and holding ponds. The major modification would be removing the existing cold ESP and installing a common plenum to distribute the flue gas to the scrubber trains. The use of this common plenum and four scrubber trains will allow this system to be easily turned down by simply closing off any combination of scrubber trains.

The materials of construction required for this process have not been specified.

Environmental Considerations

Essentially no information has been published listing the NO_x removal efficiency and the sensitivity of this removal efficiency to changes in the flue gas composition and operating conditions in the absorbers.

The generation of NO_3^- salts in this process represents a significant waste disposal problem since these extremely soluble NO_3^- would be considered a secondary pollutant. The treatment options for the wastewater stream would be either desiccation and disposal in a landfill or some form of biological wastewater treatment. However, neither of these options would be economically attractive.

Critical Data Gaps and Poorly Understood Phenomena

There is insufficient information available to discuss the critical data gaps in detail or discuss the poorly understood phenomena and hence only the following major critical data gaps are listed.

1. Equipment operating conditions and sizes
2. MnO_4^- regeneration section
3. Stream flow and compositions
4. Estimated capital and operating costs
5. Raw material, energy, and operation requirements
6. Pilot-plant data

Advantages and Disadvantages

Although sufficient information has not been published to enable a complete listing of the technical advantages and disadvantages for this process, the following advantages and disadvantages are apparent at the present time.

Advantages

1. Achieves >90% NO_x removal efficiency
2. Produces a potentially marketable byproduct (Na_2SO_4)
3. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

1. Forms secondary source of pollution (wastewater NO_3^- salts)
2. Requires significant amounts of energy for the regeneration step
3. Has not been tested on coal-fired flue gas
4. Uses significant amounts of stainless steel or exotic materials for process equipment
5. Requires flue gas reheat for plume buoyancy
6. Requires an expensive liquid-phase oxidant

MORETANA CALCIUM PROCESS - WET, OXIDATION-ABSORPTION-REDUCTION (NO_x-SO_x)

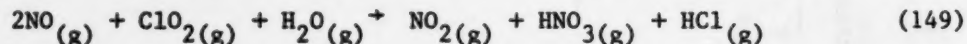
Process Description and Principles of Operation (17, 56)

This process was jointly developed by Fuji Kasui Engineering Company and Sumitomo Metal Industries as a modification to their original Na-based simultaneous SO₂-NO_x removal system. The process description and operation is very similar to the original process with the major modification being the replacement of Na⁺ ions by Ca⁺⁺ ions and thus using lime or limestone as a raw material rather than expensive NaOH. This process is also a wet, oxidation-absorption-reduction system using ClO₂ for the gas-phase oxidation of NO to NO₂. Unfortunately, this gas-phase oxidation also results in the formation of undesirable NO₃⁻ and Cl⁻ salts in the scrubbing solution.

The overall process consists of five basic steps including (1) pre-scrubbing, (2) gas-phase oxidation, (3) simultaneous SO₂-NO_x absorption, (4) byproduct sludge removal, and (5) byproduct NO₃⁻ removal. A block flow diagram detailing these various steps for the Moretana Calcium process is shown in Figure 22.

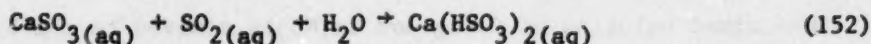
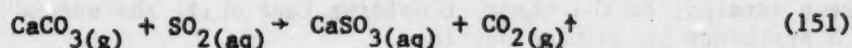
The flue gas from the air heater passes through a prescrubber counter-currently to an H₂O-based scrubbing solution which is assumed to remove 90% of the particulates and essentially all of the HCl in the flue gas. As the flue gas passes through the prescrubber it is also adiabatically cooled from 150°C (300°F) to 53°C (127°F) and humidified by the evaporation of H₂O from the scrubbing solution. The liquid effluent from the prescrubber drops to a holding tank from which most of the solution is recirculated through the prescrubber after makeup H₂O has been added. The remaining liquid is purged and pumped to a centrifuge where the flyash is removed. This flyash is sent to a waste disposal area, while the centrate is recycled to the prescrubber holding tank.

The flue gas, after passing through a mist eliminator, enters the flue gas duct and is injected with ClO₂. This ClO₂ is generated onsite and is injected at a rate of 10% in excess of the stoichiometric requirement. With the proper design of the injection system, the ClO₂ selectively oxidizes the NO by the following reaction.

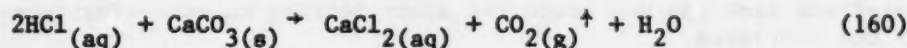
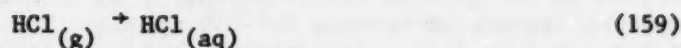
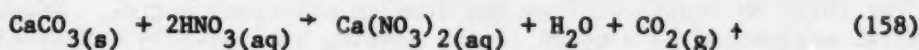
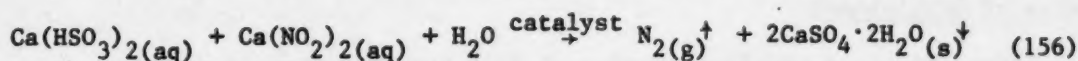
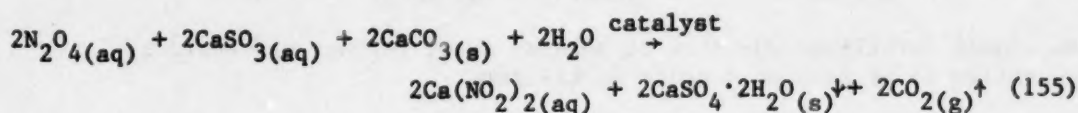


This gas-phase reaction occurs very rapidly and completely oxidizes the NO to NO₂ and HNO₃.

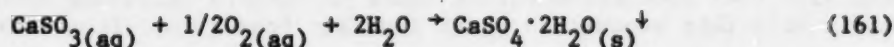
The oxidized flue gas is then passed countercurrently to a limestone slurry in a "Moretana" plate tower absorber. The limestone slurry at a pH of approximately 5.5 is a mixture of Ca salts, mainly CaSO₃ and CaCO₃, and a catalyst to aid in the reduction of NO_x. As this limestone slurry passes through the absorber, the SO₂ is stripped from the flue gas and the following reactions occur in the scrubbing solution.



At the same time the gases formed from the oxidation of NO are also absorbed from the flue gas stream and undergo the following hypothesized reactions.



Secondary reactions also occur in the absorber; for example, O_2 from the flue gas is absorbed into the scrubbing solution and causes the oxidation of CaSO_3 to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

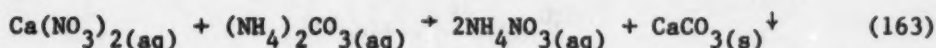
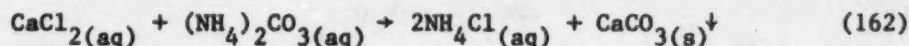


However, this oxidation of the $\text{SO}_3^{=}$ ion in the Ca system is not as serious a problem as in the Na-based systems, since CaSO_3 is relatively insoluble in the scrubbing solution. Hence, most of the CaSO_3 is not present in the solution where it can be oxidized. After passing through a mist eliminator, the cleaned flue gas is reheated and exited through the stack.

The liquid effluent from the absorber drops into a holding tank from which most of the slurry is recirculated through the absorber. The remaining portion of the slurry is pumped to a centrifuge where the relatively insoluble CaSO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are separated from the soluble CaCl_2 and $\text{Ca}(\text{NO}_3)_2$. The

solids removed in the effluent slurry centrifuge (the CaSO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are sent to a byproduct disposal area and dumped. The centrate containing the soluble Ca salts is split into two streams, the largest of which is pumped to the limestone slurring section to transport makeup limestone and makeup catalyst to the absorber holding tank while the second stream is purged to a byproduct production section.

This mixed solution of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ removed to the byproduct section can be treated by either simply drying the solution to produce CaCl_2 or reacting the solution with ammonium carbonate $\text{[(NH}_4)_2\text{CO}_3]$ or $(\text{NH}_4)_2\text{SO}_4$ to produce a liquid fertilizer. The production of liquid fertilizer involves pumping the Ca salt solution to a double decomposition reactor and mixing $(\text{NH}_4)_2\text{CO}_3$ with the salt solution where the following reactions occur.



This liquid fertilizer may then be sold as is or further processed by evaporation to be sold as a solid fertilizer.

Status of Development

Since this is a modified version of Fuji Kasui-Sumitomo's original Na-based wet, simultaneous SO_2 - NO_x removal process, this process has not been as extensively tested as the original Na-based system. Testing of this Ca-based system was begun in 1975 in a bench-scale unit treating 500 Nm^3/hr (0.16 MW equiv) of flue gas from an oil-fired boiler. After this initial evaluation on a bench scale, testing has recently (1976) begun on a 25,000 Nm^3/hr (8.3 MW equiv) prototype unit treating flue gas from a sintering furnace containing 400-850 ppm SO_2 , 180-250 ppm NO_x , 16-20% O_2 , and 1-3 g/ Nm^3 of dust. In addition, bench-scale testing on synthetic coal-fired flue gas was conducted after testing on sintering furnace flue gas was initiated.

Although this process has not been tested on flue gas from a coal-fired boiler, the developers believed that the use of a Moretana plate tower as a prescrubber to remove the increased particulates and Cl^- associated with coal combustion before these pollutants reach the absorber would enable this process to treat flue gas from a coal-fired boiler.

The next stage of development would be either a pilot-plant or small prototype unit to test the ability of this system to handle flue gas from either an oil- or coal-fired boiler.

Background of Process Developers

In the past 20 yr Fuji Kasui has been active in the development of pollution control equipment and processes. In the early 1970's Fuji Kasui undertook the development of processes to remove SO_2 and NO_x from combustion exhaust gas and later began joint research with Sumitomo for development of

processes using the Moretana absorption tower. This involvement began with the design and engineering of the Moretana absorption tower and the later use of this absorption tower both for a particulate removal and FGD applications. One of these early applications was for the desulfurization of heavy oil-fired flue gas at a Sumitomo plant in 1971. In May 1973 a prototype plant (20 MW equiv) was started up using a CaO-scrubbing process for desulfurization and a new test plant for simultaneous SO₂ and NO_x removal was begun.

At the present time 12 desulfurization and 7 combination desulfurization-denitrification plants (10-40 MW equiv) are already operating (although only 2 of these SO₂-NO_x processes use the Ca-based system) and hence at the present time Fuji Kasui-Sumitomo probably has more experience in flue gas denitrification than any other company.

No American company has been licensed by Fuji Kasui-Sumitomo to market their process in the U.S. However, Sumitomo does have a liaison office in New York City through which inquiries about this process are handled.

Published Economic Data

The following estimated costs for the Moretana Calcium process are based on treating 500,000 Nm³/hr of flue gas from a heavy oil-fired boiler containing 1,500 ppm SO₂, 200 ppm NO_x, 4% O₂, and 0.1 g/Nm³ of dust and a desulfurization and denitrification efficiency of 99 and 90% respectively. The total capital investment and the revenue requirements (assumed basis: Japan and 1976 costs) for the above-mentioned plant are estimated (17) by the developers to be 2500 million yen and 7009 yen/kl of oil respectively. If 300 yen/\$ and 3000 Nm³/hr/MW are assumed, this corresponds to an estimated capital investment of \$50/kW of capacity and an estimated revenue requirement of 5.78 mills/kWh.

Raw Materials, Energy, and Operation Requirements

Other than the crushed limestone for the absorbing solution which is readily available, the major raw materials required are H₂SO₄ and the chemicals required to generate ClO₂ (these chemicals are considered proprietary). In addition, lesser amounts of makeup catalyst will also be needed. The quantities of these raw materials have not been published.

The energy requirements such as fuel oil for flue gas reheating, steam, H₂O, and electricity have also not been made available.

The operating manpower and maintenance requirements for this process have not been published.

Technical Considerations

The Moretana Calcium process uses ClO₂ for the gas-phase oxidation of NO and a CaSO₃ scrubbing solution, containing a dissolved catalyst to aid in the absorption of the resulting NO₂. Since ClO₂ cannot be stored but must be generated onsite, the major process control problem will be the control of the ClO₂ generation and injection system. If ClO₂ is injected

in less than stoichiometric amounts, the NO_x removal efficiency will decline proportionally and if it is injected in more than stoichiometric amounts, excess ClO_2 will contribute excess Cl^- ions to the scrubbing solution and will also increase operating expenses since the generation of ClO_2 is one of the major costs.

The use of ClO_2 as the gas-phase oxidant also complicates the process control scheme for another reason. Since ClO_2 is generated by chemical reaction and requires significant time periods (15-30 min) to adjust to changing NO_x levels in the flue gas, this process will have difficulty cycling with changing flue gas NO_x concentrations.

As is typical for most of the oxidation-absorption-reduction processes, the NO_x removal efficiency is relatively insensitive to the inlet gas composition. In the case of the Moretana Calcium process this insensitivity is due to several factors, the most important of which is the relative insolubility of the CaSO_3 in the scrubbing solution. This insolubility prevents most of the SO_3^{2-} , formed by the absorption of SO_2 from the flue gas, from being oxidized to SO_4^{2-} by flue gas O_2 absorbed into the scrubbing solution and hence more of the SO_3^{2-} ion is available for reducing the NO_x . A second major reason for this insensitivity to flue gas composition is that only a portion of the absorbed NO_x is reduced by the SO_3^{2-} to molecular N_2 . Thus the relative insensitivity of this process to the flue gas composition is due to the use of insoluble CaSO_3 which decreases the loss of the SO_3^{2-} ion by oxidation and also because of the small amount of SO_3^{2-} required since only part of the absorbed NO_x is reduced to molecular N_2 .

Although the use of relatively insoluble CaSO_3 minimizes the oxidation of the SO_3^{2-} ion in the scrubbing solution, this insolubility of the SO_3^{2-} ion necessitates the use of a dissolved catalyst to aid in the absorption of the NO_x . Apparently for proprietary reasons, the process developers have not published detailed information concerning this catalyst. However, it is probably a mixture of copper (Cu) ions and other proprietary additives. A similar mixture is used in some of the other oxidation-absorption-reduction processes and the mechanism by which it aids NO_x removal is not well understood.

The Moretana plate tower is used for both the prescrubber and the absorber in this process. The Moretana plate tower is very similar to a sieve tray absorber except that it has no weirs or downcomers as can be seen in Figure 23. As the liquid and gas pass countercurrently to each other in the tower, there is an alternating flow of first liquid and then gas through the perforations in each plate. As the height of liquid on a plate increases, the weight of the liquid overcomes the force of the gas pushing through the perforations and the liquid displaces the gas and flows through the first plate to the lower plate. As the liquid height on the first plate decreases, the gas pressure forces the displacement of the liquid and the gas flows through the perforations in the plate. This alternating pulsing of first liquid and then gas through the plate gives the gas-liquid contact required for simultaneous SO_2 - NO_2 absorption and gives the Moretana plate tower advantages over other types of absorbers. The developers claim this design allows the Moretana plate tower to handle higher superficial gas velocities which reduces the size of the absorber required in a particular situation.

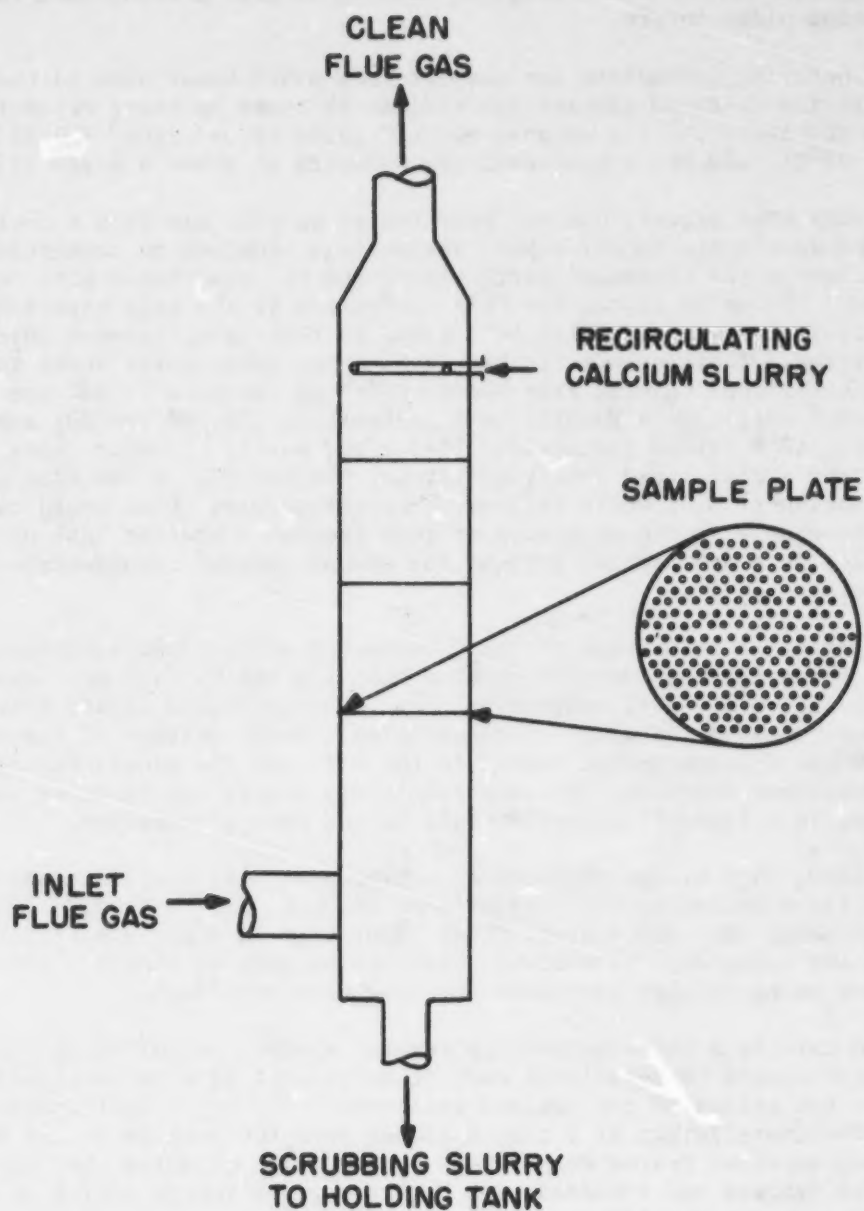


Figure 23. "Moretana" Plate Tower (110).

This constantly and violently moving gas-liquid contact area is also claimed by the developers to prevent both the formation and the buildup of scale inside the tower and also the plugging associated with conventional FGD systems using plate towers.

The operating parameters for the Moretana plate tower used as the absorber in the Ca-based process are similar to those in their conventional limestone FGD system, i.e., an absorber L/G ratio of 3-7 l/Nm³ (20-45 gal/kaft³ at 127°F), and the superficial gas velocity of about 4 m/sec (13 ft/sec).

Although this process has not been tested on flue gas from a coal-fired boiler, the developers do not expect any serious problems in converting this system to handle the increased particulates and Cl⁻ associated with coal combustion. The major reason for this confidence is the wide experience in applying their FGD system, which is similar to their simultaneous SO₂-NO_x removal system. Their desulfurization system has been tested under various operating conditions ranging from heavy oil-fired furnaces (1,400 ppm SO₂ and 0.2 g/Nm³ dust), to a Rhodine salt incinerator (28,900 ppm SO₂ and 0.5 g/Nm³ dust), to a refuse incinerator (1-3 g/Nm³ dust). However, when treating flue gas from a coal-fired boiler containing 600 ppm NO_x in the flue gas, the consumption of ClO₂ would increase proportionately. This would cause a significant change in the economics of this process since the cost of generating ClO₂ is a substantial part of the annual revenue requirements for this process.

Apparently at this stage in the development of Ca-based scrubbing process, it has not been decided whether removing the Cl⁻ and NO₃⁻ salts as a solid salt mixture or converting them to an NH₃-based liquid fertilizer is the best method of disposal of these salts. Since neither of these byproducts has a large market demand in the U.S. and the manufacturing of liquid fertilizer byproduct consumes (NH₄)₂CO₃, simply drying these salts and placing in a landfill probably would be the best alternative.

The CaSO₄·2H₂O sludge produced as a byproduct will contain numerous salt impurities including SO₃²⁻, bisulfates (HSO₄⁻), Cl⁻, and NO₃⁻. Since CaSO₄·2H₂O which does not contain these impurities is readily available in the U.S., any CaSO₄·2H₂O formed will probably be used as landfill material rather than being further processed for sale as a byproduct.

Since this is a wet simultaneous removal system, retrofitting existing power plants should be relatively easy if sufficient land is available nearby for the siting of the process equipment. The major modification would be the installation of a common plenum from the boilers or the ESP to the four scrubber trains on a 500-MW boiler. The existing cold ESP would probably be removed and replaced with Moretana plate towers acting as pre-scrubbers to remove the Cl⁻ as well as the flyash.

The use of a common plenum and four absorber trains will allow this system to be easily turned down from 100% to 75, 50, or 25% by simply closing off any combination of scrubber trains.

Since the use of ClO_2 as an oxidizing agent will inject relatively high (2000 ppm) concentration of Cl^- ions in the scrubbing solution, most of the process equipment and piping will need to be elastomer-lined carbon steel to prevent pitting corrosion associated with circulating Cl^- solutions. Exceptions to this elastomer lining of process equipment and piping include the inlet flue gas ducts which will be constructed of Inconel 625 to prevent corrosion by the flue gas, and the absorber and absorber pumps which will be made from 316L stainless steel.

Environmental Considerations

During bench-scale testing of this process on a $500 \text{ Nm}^3/\text{hr}$ unit (0.16 MW equiv) treating flue gas from a heavy oil-fired boiler (1500 ppm SO_2 , 200 ppm NO_x , 4% O_2 , $0.1 \text{ g}/\text{Nm}^3$ dust), SO_2 and NO_x removal efficiencies of 95 and 90%, respectively, were attained. The SO_2 , which is absorbed as the SO_3^- ion, is oxidized to SO_4^- either by reducing the absorbed NO_x to molecular N_2 or by reacting with O_2 absorbed into the solution. Approximately 30% of this SO_3^- to SO_4^- oxidation is assumed to occur in the absorber with the remainder occurring in the oxidizer of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ production section. The absorbed SO_2 is thus recovered in the form of byproduct $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ which along with the flyash will probably be used as a landfill material. Some of the absorbed NO_x is reduced to molecular N_2 by oxidation of the SO_3^- ion while the remainder is removed as NO_3^- salts, either as a solid salt mixture or as an ammonium nitrate (NH_4NO_3) solution.

The NO_x removal efficiency is dependent on the amount of ClO_2 injected. If the injection of ClO_2 declines below the 10% excess rate specified by the process developers, the NO_x removal efficiency will drop below 90%. A complete failure of the ClO_2 generation equipment will result in only approximately 5% of the NO_x being removed. The SO_2 removal efficiency, which is independent of the amount of ClO_2 injected or the inlet flue gas conditions, will remain >95%.

The ClO_2 used to oxidize the NO in the flue gas is the only significant work hazard associated with this process. This gas is a very strong oxidant and can be dangerous if workers are exposed to even low concentrations.

Critical Data Gaps and Poorly Understood Phenomena

Listed below are the critical data gaps for the Moretana Ca-based system. In addition preliminary engineering assumptions are listed for some of these critical data gaps.

1. Stream compositions and operating conditions in each piece of process equipment
2. Percent of NO_x reduced to molecular N_2 (assumed to be 50%)
3. Oxidation of SO_3^- ion in absorber
4. Raw material, energy, maintenance, and manpower requirements and costs
5. Identity and concentration of catalyst (assumption: Cu ion and some proprietary additives)

The sequence of reactions occurring in the scrubbing solution to reduce the NO_x to molecular N_2 is not completely understood with Fuji Kasui-Sumitomo apparently only providing overall reactions. The sequence is hypothesized by others (33) to be the following: The NO_2 apparently forms the dimer molecule and enters the solution in this form. From a literature survey the absorbed dimer molecule forms both NO_2^- and NO_3^- ions in the scrubbing solution. The reduction of the NO_2^- ion to molecular N_2 by the combined action of the HSO_3^- ion and the dissolved catalyst, which is a major advantage for this process, is not well understood and only the overall reaction is supplied by Fuji Kasui-Sumitomo (reaction 156).

Advantages and Disadvantages

Since this is a wet simultaneous SO_2 - NO_x process, it has certain advantages and disadvantages over the dry NO_x processes and some over other wet nonoxidation processes. The advantages and disadvantages are listed below.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Is a slight modification of a commercially available FGD system
4. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

1. Requires significant amounts of energy for the regeneration step
2. Has not been tested on coal-fired flue gas
3. Incorporates design features which may present significant process control problems
4. Uses significant amounts of stainless steel or exotic materials for process equipment
5. Requires flue gas reheat for plume buoyancy
6. Requires an expensive gas-phase oxidant

MORETANA SODIUM PROCESS - WET, OXIDATION-ABSORPTION-REDUCTION ($\text{NO}_x\text{-SO}_x$)

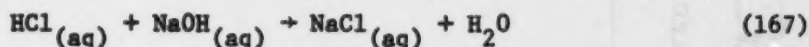
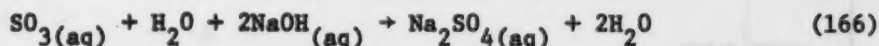
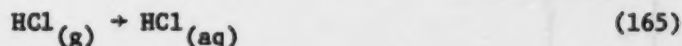
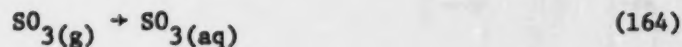
Process Description and Principles of Operation (5, 17)

The Moretana Sodium process jointly developed by Fuji Kasui-Sumitomo uses ClO_2 for the gas-phase oxidation of NO to NO_2 and an $\text{NaOH-Na}_2\text{SO}_3$ solution to absorb both SO_2 and NO_2 . The overall process is made up of six major sections including (1) prescrubbing, (2) gas-phase oxidation, (3) SO_2 and NO_x absorption, (4) SO_3^{2-} oxidation, (5) byproduct Na_2SO_3 recovery, and (6) wastewater treatment. A more detailed outline of this process can be seen in the block flow diagram given in Figure 24.

Fuji Kasui-Sumitomo also has a Ca-based process which is based on similar technology except limestone is used as the raw material. The primary differences between these two processes are the operating costs involved. For this reason Fuji Kasui-Sumitomo recommend their Na-based system only for relatively small installations treating $<100,000 \text{ Nm}^3/\text{hr}$ (33.5 MW equiv) and more specifically for those sites burning a gaseous or liquid fuel. Thus, for most U.S. applications, the Ca-based process is more important since it will be used for large coal-fired power plants.

The use of ClO_2 in the Moretana Sodium process to chemically oxidize the NO overcomes the major problem of wet denitrification systems, i.e., the relative insolubility of NO in aqueous solutions, and substantially reduces the equipment requirements for the denitrification process. This is readily apparent from a comparison of the block flow diagram for this process shown in Figure 24 with the block flow diagrams given for the other types of wet processes. The gas-phase oxidation of NO with ClO_2 , however, in addition to the increased expense for gaseous ClO_2 , also results in the formation of undesirable NO_3^- and Cl^- salts in the scrubbing solution.

The flue gas from the air heater passes through a Moretana prescrubber countercurrently to an NaOH solution. This solution is assumed to remove 90% of the particulates and essentially all of the HCl from the flue gas. At the same time the flue gas is adiabatically cooled from 150°C (300°F) to 53°C (127°F) and humidified by the evaporation of H_2O from the scrubbing solution. The reactions occurring in the prescrubber, due to the absorption of SO_3 and HCl , would include the following:



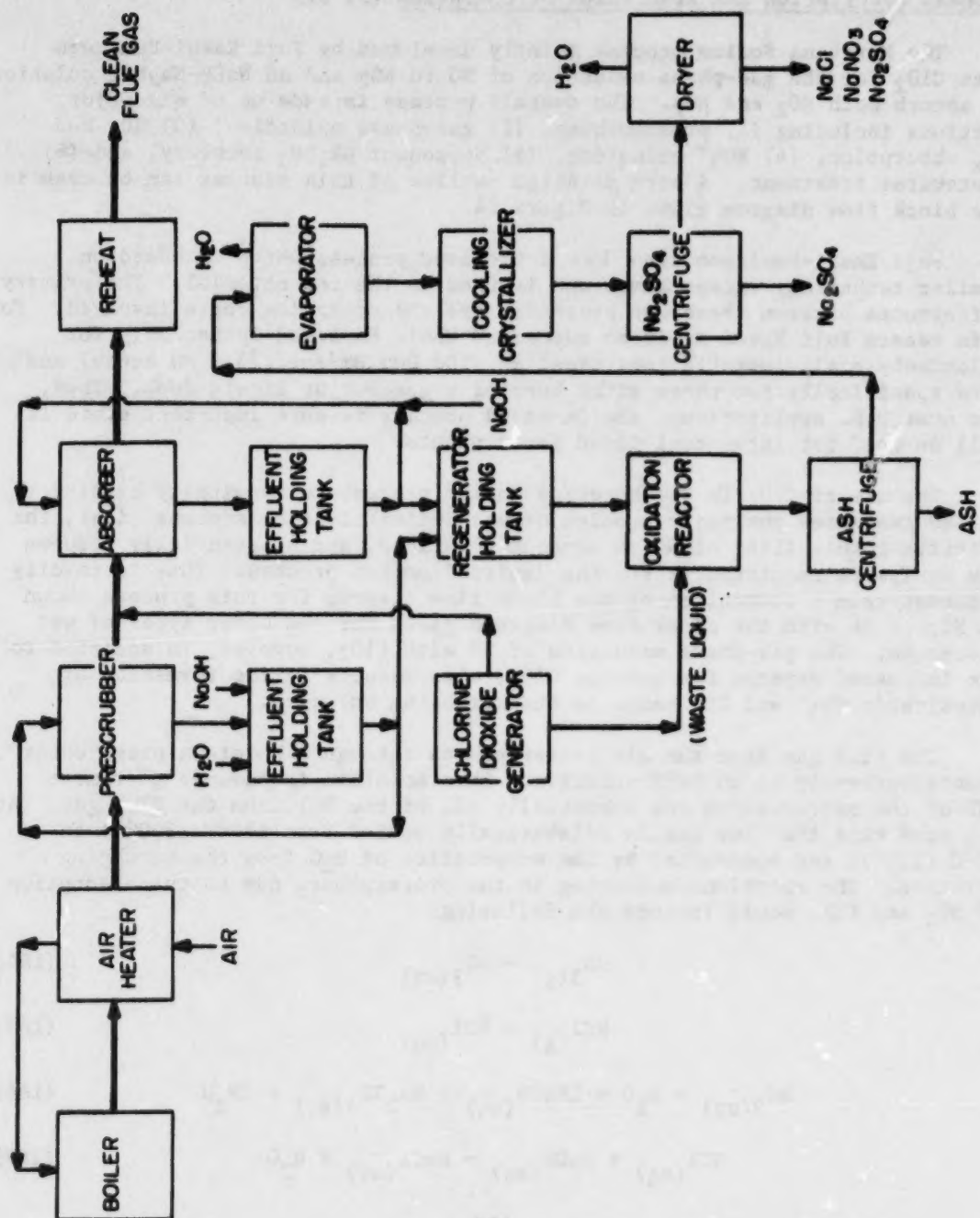
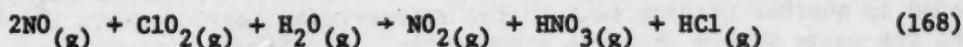


Figure 24. Flow Diagram of Moretana Sodium Process.

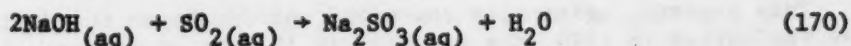
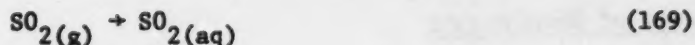
The liquid effluent from the prescrubber drops into a holding tank where makeup H₂O and makeup NaOH are added to replace these raw materials consumed during passage through the prescrubber. Most of the solution is recirculated through the prescrubber but a small portion is removed as a purge stream to prevent the buildup of flyash and the Na salts in the prescrubber solution. This purge stream is pumped to a holding tank in the regeneration section for further processing.

The flue gas passes through a mist eliminator at the top of the prescrubber and is injected with a weak (3-5%) ClO₂ gas stream in the flue gas duct prior to entering the absorber. The ClO₂ is generated onsite and is injected in the amount of 10% in excess of the stoichiometric requirement. With a properly designed injection system, the ClO₂ selectively oxidizes NO by the following reaction:

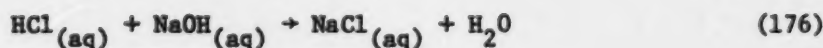
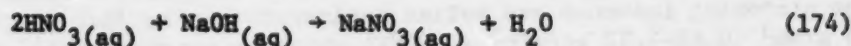
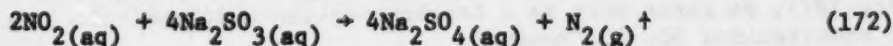


This gas-phase reaction is very rapid (0.3 sec) and essentially goes to completion. The reaction is also very selective, in that none of the SO₂ is oxidized by the ClO₂.

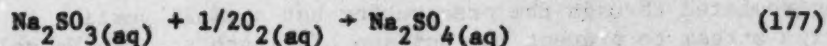
Immediately after the injection of the ClO₂, the flue gas passes countercurrently to a slightly basic (pH of 7.2-7.4) Na-based scrubbing solution in a Moretana plate tower. As the solution passes through the absorber, the SO₂ is rapidly stripped from the flue gas and the following reactions occur in the solution:



At the same time the gases formed from the oxidation of NO in reaction (168) are also absorbed from the flue gas stream and undergo the following hypothesized reactions:



In addition to these primary reactions, a secondary reaction occurs as the flue gas passes through the absorber. Flue gas O_2 , which is readily absorbed into the scrubbing solution, causes the following undesirable side reaction:



This loss of SO_3^{2-} ion by oxidation can be a substantial problem at higher flue gas O_2 concentrations. After passing through a mist eliminator, the flue gas from the top of the absorber is reheated and exits through the stack.

The spent scrubbing solution is removed from the bottom of the Moretana plate tower and sent to an effluent holding tank. Most of this solution is removed and recycled to the absorber after makeup $NaOH$ has been added. The remaining portion of the solution, containing mainly Na_2SO_4 and Na_2SO_3 , is pumped to another holding tank in the regeneration section where it is mixed with the purge stream from the prescrubber. The liquid effluent from this holding tank in the regeneration section and the liquid waste from the ClO_2 generating system are sent to an oxidation reactor where air is injected to oxidize any remaining SO_3^{2-} to SO_4^{2-} . The solution from the oxidizer is pumped to a centrifuge where the flyash is removed, and then on to an evaporator where indirect steam heating is used to concentrate the solution. This concentrated solution is passed to a cooling crystallizer where Na_2SO_4 , which is the largest constituent and the least soluble of the Na salts in the solution, is precipitated and then recovered as a byproduct in a centrifuge. The mother liquor from this centrifuge is sent to a dryer where the liquor is desiccated and a mixture of Na salts is recovered.

Status of Development

This process, originally conceived and developed for dust removal and desulfurization in 1970, was modified in 1973 to simultaneously remove NO_x from flue gas. The only significant modification required to make this change to a simultaneous SO_2 - NO_x removal system was the addition of the ClO_2 generation and injection system. At the present time five prototype units (10-40 MW) using the Fuji Kasui-Sumitomo Na-based simultaneous SO_2 - NO_x removal process are treating flue gas from heavy oil-fired boilers (typically containing 1500 ppm SO_2 , 200 ppm NO_x , 4% O_2 , and 0.1 g/ Nm^3 of dust). A unit (20 MW equiv) at the Sumitomo plant in Amagasaki City has been operating since 1973, at first only as a desulfurization unit and then later modified for simultaneous SO_2 - NO_x removal.

Although this process has not been tested on flue gas from a coal-fired boiler, it has been applied to dust removal and desulfurization of flue gas from sintering furnaces and refuse incinerators with dust loadings as high as 1-3 g/ Nm^3 (0.41-1.22 gr/sft³ at 60°F) which is approximately one-fifth the dust levels expected from coal-fired boilers. It has also been used for

desulfurization of the exhaust gas containing as much as 3% SO_x . Once an initial prescrubber has been added to remove the increased levels of Cl^- in the flue gas, this process would probably be capable of handling coal-fired flue gas.

Background of Process Developer

In the past 20 yr, Fuji Kasui has been active in the development of pollution control equipment and processes. In the early 1970's, Fuji Kasui undertook the development of processes to remove SO_2 and NO_x from combustion exhaust gas and later began joint research with Sumitomo for development of processes using the Moretana absorption tower. This involvement began with the design and engineering of the Moretana absorption tower and the later use of this absorption tower both for a particulate removal and FGD applications. One of these early applications was for the desulfurization of heavy oil-fired flue gas at a Sumitomo plant in 1971. In May 1973 a prototype plant (20 MW equiv) was started up using a CaO scrubbing process for desulfurization and a new test plant for simultaneous SO_2 and NO_x removal was begun.

At the present time 12 desulfurization plants and 7 combination desulfurization-denitrification plants (10-40 MW equiv) are already operating and hence at the present time Fuji Kasui-Sumitomo probably have more experience in flue gas denitrification than any other company.

No American company has been licensed by Fuji Kasui-Sumitomo to market their process in the U.S. However, Sumitomo does have a liaison office in New York City through which inquiries about this process are handled.

Published Economic Data

The following estimated costs for the Moretana Sodium process are based on 62,000 Nm^3/hr of flue gas from a heavy oil-fired boiler, which contains 1500 ppm SO_2 , 200 ppm NO_x , 4% O_2 , and 0.1 g/ Nm^3 of dust, with a 99% SO_2 and 90% NO_x removal efficiency respectively. The total capital investment and the revenue requirements have been estimated (17) by Fuji Kasui-Sumitomo (assumed basis--Japan and 1976 costs) as 830 million yen and 11,160 yen/kl of oil respectively. If 300 yen/\$ and 3000 $\text{Nm}^3/\text{hr}/\text{MW}$ are assumed, these values correspond to an estimated capital investment of \$134/kW of installed capacity and a revenue requirement of 8.9 mills/kWh.

Raw Materials, Energy, and Operation Requirements

The major raw material requirements given below are based on treating 62,000 Nm^3/hr of oil-fired flue gas containing 1500 ppm SO_2 and 200 ppm NO_x . The desulfurization and denitrification efficiencies were assumed to be 95% and 90% respectively.

<u>Raw material</u>	<u>Quantity</u>
NaOH	204 kg/day

The utility requirements on the same basis as listed above are:

Utility	Quantity
Electricity	100 kW
Steam	32,500 kg/day
Fuel oil	290 kg/day

The estimated manpower to operate and maintain this system has not been published.

Technical Considerations

The Moretana Sodium process, using ClO_2 for the gas-phase oxidation of NO and an Na_2SO_3 scrubbing solution to absorb the resulting NO_2 , appears to require fewer pieces of process equipment than the other oxidation processes. As a result the process control for this system should be less difficult than that required for the reduction processes. Since ClO_2 cannot be stored but must be generated onsite, the major process control problem for this process will be the ClO_2 generation and injection system. If the ClO_2 is injected in less than stoichiometric amounts, the NO_x removal efficiency will decline and, if injected in more than stoichiometric amounts, excess ClO_2 will contribute excess Cl^- ions to the scrubbing solution and increase operating costs for both ClO_2 generation and makeup NaOH .

The use of ClO_2 as the gas-phase oxidant also complicates the process control scheme for another reason. Since ClO_2 is generated by chemical reaction and requires significant time periods (15-30 min) to adjust to changing NO_x levels in the flue gas, this process will have difficulty cycling with changing flue gas NO_x concentrations.

The NO_2 removal efficiency is relatively insensitive to the inlet gas composition providing that the $\text{SO}_2:\text{NO}_x$ mol ratio is relatively high (a mol ratio of 5 is required for 90% NO_x removal). The major reason for the sensitivity of this process to the SO_2 concentration in the flue gas is that although only approximately 50% of the absorbed NO_x is reduced by the $\text{SO}_3^{=}$ ion to molecular N_2 , substantial amounts of $\text{SO}_3^{=}$ (absorbed SO_2) in the solution are lost due to oxidation by flue gas O_2 . For NO_x removal efficiencies of less than 90% and/or lower flue gas O_2 levels (<4-5%) the required $\text{SO}_2:\text{NO}_x$ mol ratio would be lower. Thus for coal-fired boilers, particularly boilers fired with low-S western coal, high NO_x removal efficiencies may be difficult.

The Moretana plate tower, which was developed by Fuji Kasui-Sumitomo, is used for both the prescrubber and the absorber in this process. The Moretana plate tower is very similar to a sieve tray absorber except that it has no weirs or downcomers as can be seen in Figure 23. As the liquid and gas pass countercurrently to each other in the tower, there is an alternating flow of first liquid and then gas through the perforations in each plate. As the

height of liquid on a plate increases, the weight of the liquid overcomes the force of the gas pushing through the perforations and the liquid displaces the gas and flows through the first plate to the lower plate. As the liquid height on the first plate decreases, the gas pressure forces the displacement of the liquid and the gas flows through the perforations in the plate. This alternating pulsing of first liquid and then gas through the plate gives the gas-liquid contact required for simultaneous $\text{SO}_2\text{-NO}_2$ absorption. In addition, the developers claim this design allows the Moretana plate tower to handle higher superficial gas velocities and thus reduces the size of the absorber required in a particular situation.

For Fuji Kasui-Sumitomo's Na scrubbing process, the Moretana plate tower absorber is operated at an L/G ratio of $2.0\text{-}3.5 \text{ l/Nm}^3$ ($10\text{-}25 \text{ gal/kaft}^3$ at 127°F) and a superficial gas velocity of $3\text{-}5 \text{ m/sec}$ ($10\text{-}16.5 \text{ ft/sec}$). The pressure drop through the Moretana plate tower operating under these conditions (i.e., a superficial gas velocity of 4.5 m/sec and L/G ratio of 25) at a pilot plant averaged 200 mm of H_2O .

The major disadvantage associated with this process is the extensive energy requirement for the regeneration section. These high energy requirements, particularly the steam needed for the evaporators, are a direct result of the oxidation of NO by ClO_2 . The conversion of NO to NO_2 results in the formation of NO_3^- salts when the NO_2 is absorbed into the scrubbing solution. Further complicating the regeneration section is the formation of Cl^- salts from the ClO_2 used to oxidize NO. Not only is this NaCl salt extremely soluble and thus difficult to remove, but it also consumes expensive NaOH. Since the NO_3^- salts are also extremely soluble, the process developers have suggested a two-stage desiccation scheme using steam evaporators to recover these salts. Unfortunately with increases in primary energy costs, the use of steam to evaporate this purge stream from the regeneration section can only lead to high and steadily increasing operating costs.

Recently the developers have begun tests using O_3 instead of ClO_2 for the gas-phase oxidation of NO. Although the use of O_3 eliminates the problems associated with the formation of Cl^- in the scrubbing solution, O_3 has two major disadvantages when compared with ClO_2 . First, 1 mol of ClO_2 will oxidize twice as many mols of NO as 1 mol of O_3 and secondly, the unit cost of O_3 is approximately four times as expensive as that of ClO_2 system for its wet simultaneous $\text{SO}_2\text{-NO}_x$ removal systems.

Although this process has not been tested on flue gas from a coal-fired boiler, the developers do not expect any serious problems in converting this system to handle the increased particulates and Cl^- associated with coal combustion. The major reason for this confidence is the wide experience in applying their FGD system which is very similar to their simultaneous $\text{SO}_2\text{-NO}_x$ removal system. Their desulfurization system has been tested under various operating conditions ranging from heavy oil-fired furnaces (1400 ppm SO_2 and 0.2 g/Nm^3 dust), to a Rhodine salt incinerator (28,900 ppm SO_2 and

0.5 g/Nm³ dust), to a refuse incinerator (1-3 g/Nm³ dust). However, the increased levels of NO_x in flue gas from a coal-fired boiler will sharply increase the consumption of ClO₂ and this will further aggravate the problem of Cl⁻ salts production and its associated consumption of expensive NaOH.

Since this is a wet simultaneous removal system, retrofitting this system on existing power plants should be relatively easy if sufficient land is available nearby for the siting of the process equipment. The major modification to the existing plant would be the installation of a common plenum from the boilers or the ESP to the two scrubber trains on a 500-MW boiler. The existing cold ESP would probably be removed and replaced with Moretana plate towers acting as prescrubbers to remove the Cl⁻ as well as the flyash.

The use of a common plenum and four absorber trains will allow this system to be easily turned down from 100% to 75, 50, or 25% by simply closing off any combination of scrubber trains.

Since the use of ClO₂ as an oxidizing agent will inject relatively high (2000 ppm) concentration of Cl⁻ ions in the scrubbing solution, most of the process equipment and piping will need to be elastomer-lined carbon steel to prevent pitting corrosion associated with circulating Cl⁻ solutions. Exceptions to this elastomer lining of process equipment and piping include the inlet flue gas ducts, which should be constructed of Incoloy to prevent corrosion by SO₃ in the flue gas, and the absorber and absorber pumps which should be made from 316L stainless steel.

Environmental Considerations

Over a long-term continuous operation of their prototype units (10-40 MW equiv) on heavy oil-fired boilers treating flue gas containing 1500 ppm SO₂, 200 ppm NO_x, and 4% O₂, SO₂ and NO_x removal efficiencies of 95 and 90%, respectively, were attained. The SO₂ is absorbed as an SO₃⁻ ion and partially oxidized to SO₄⁻ in the absorber either by reducing NO_x to molecular N₂ or by flue gas O₂ absorbed into the solution. The remaining SO₃⁻ ion in the solution is converted to SO₄⁻ by reaction with air in an oxidizing tower. Part of the NO_x (assumed 50%) is reduced to molecular N₂ by the SO₃⁻ ion in the scrubbing solution while the remainder is removed from the solution as NO₃⁻ salts.

The NO_x removal efficiency is directly dependent on the amount of ClO₂ injected. If the injection of ClO₂ declines below the 10% in excess of stoichiometric rate, the NO_x removal efficiency will drop below 90%. A complete failure of the ClO₂ generation equipment will result in only approximately 5% of the NO_x being removed. On the other hand the SO₂ removal efficiency will remain well above 95% since it is independent of the amount of ClO₂ injected.

A potential NO₃⁻ wastewater problem has been eliminated by the decision to evaporate the purge stream and recover the mixed Na salts as a solid. If

a market cannot be found for the Na salts, the ultimate disposal of these salts could become a problem.

The ClO_2 used to oxidize the NO in the flue gas is a very strong oxidizing agent and hence presents a significant work hazard for this process.

Critical Data Gaps and Poorly Understood Phenomena

Listed below are critical data gaps followed in some cases by the preliminary engineering assumptions used to overcome these data gaps.

1. Percent of NO_x reduced to molecular N_2 (assumed to be 50%)
2. Oxidation of Na_2SO_3 in absorber with 4% O_2 in flue gas
3. Operating conditions in the process equipment and the stream compositions
4. Maintenance and manpower requirements

Included under poorly understood phenomena for this process is the following:

The actual sequence of reactions occurring in the scrubbing solution to reduce the NO_x to molecular N_2 is not completely understood. From a literature review it is hypothesized that the NO_2 apparently forms the dimer molecule and enters the solution in this form. However, the process developers claim that NO_2 enters the scrubbing solution as NO_2 and forms only the NO_2^- ion. The resulting absorbed NO_x is apparently reduced by the SO_3^- ion to form molecular N_2 .

Advantages and Disadvantages

Since this is a wet simultaneous SO_2 - NO_x process, it has certain advantages and disadvantages, as shown below, over dry NO_x processes and some over other wet nonoxidation processes.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Produces a potentially marketable byproduct (Na_2SO_4)
4. Is a slight modification of a commercially available FGD system
5. Operates with full particulate loadings (>7 gr/sft³)

Disadvantages

1. Requires significant amounts of energy for the regeneration step
2. Has not been tested on coal-fired flue gas
3. Incorporates design features which may present significant process control problems
4. Uses significant amounts of stainless steel or exotic materials for process equipment
5. Requires flue gas reheat for plume buoyancy
6. Requires an expensive gas-phase oxidant

NISSAN PERMANGANATE PROCESS - WET, ABSORPTION-OXIDATION (NO_x)

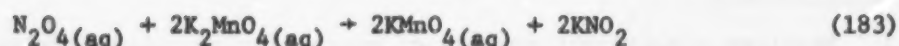
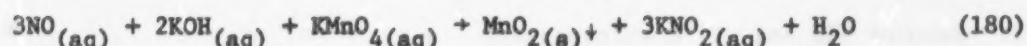
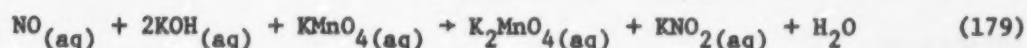
Process Description and Principles of Operation (5)

The Nissan Permanganate process was developed by Nissan Engineering, a subsidiary of Nissan Chemical Industries, Ltd. This process was originally designed to treat HNO₃ tail gas but with the installation of an FGD system prior to the denitrification system, the process, from a technical standpoint, can be adapted to fully treat power plant stack gas. The Nissan Permanganate is divided into six major sections (1) prescrubbing, (2) SO₂ absorption, (3) byproduct SO₄²⁻ formation, (4) NO_x absorption, (5) NO_x oxidation with MnO₄⁻, and (6) removal and regeneration of the MnO₄⁻. A block flow diagram of the Nissan process is shown in Figure 25. The Nissan Permanganate process is very similar to the MON Alkali Permanganate process as seen from a comparison of Figure 21.

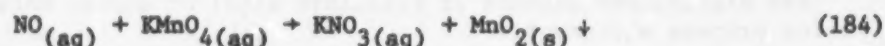
Although not mentioned by the process developers, this system is expected to require a closed-loop prescrubber section when treating flue gas from a coal-fired boiler to remove the particulates and the Cl⁻. In addition to removing 90% of the particulates and essentially all of the Cl⁻, this prescrubber also humidifies and cools the gas from 150°C (300°F) to 53°C (127°F).

The flue gas from the prescrubber enters a desulfurization system to remove most of the SO₂ and thus prevent the excessive consumption of MnO₄⁻ ion in the denitrification system. Since no specific FGD system has been mentioned by Nissan Engineering, a limestone throwaway system was assumed.

The flue gas from the limestone scrubber enters the denitrification scrubber and passes countercurrently to a KOH scrubbing solution containing KMnO₄. The NO is gradually absorbed over the length of the scrubber and undergoes the following reactions:



However, the main reaction occurring in the neutral absorbing solution is the direct oxidation of the NO by KMnO₄, i.e.,



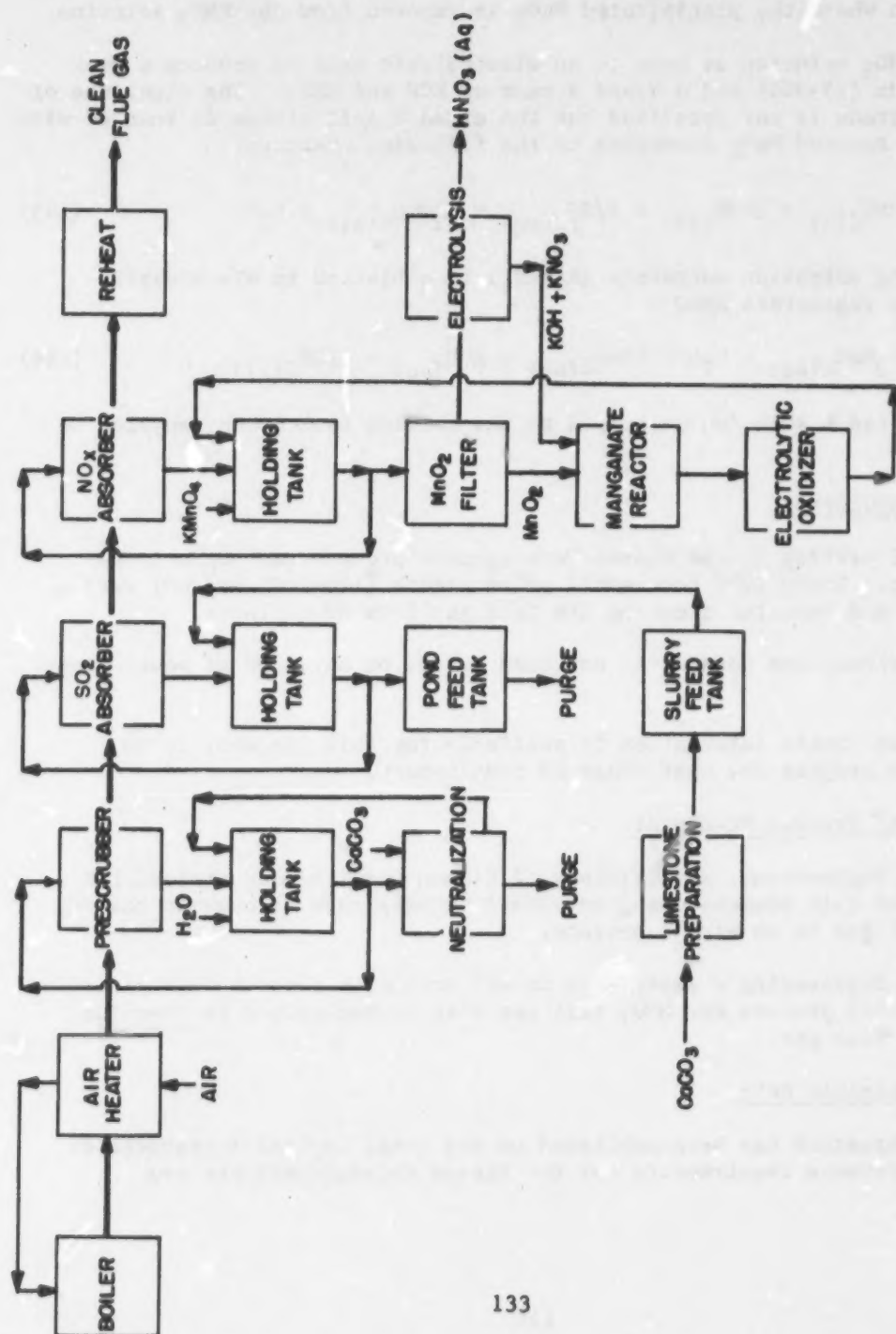
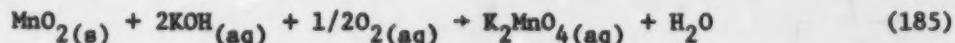


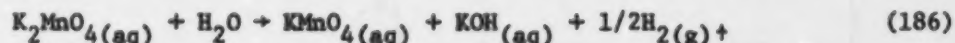
Figure 25. Flow Diagram of Nissan Engineering Process.

Gas from the scrubber is reheated and sent to the stack. The scrubbing solution drops into a holding tank from which most of the solution is recycled to the absorber after makeup KOH has been added. A small purge stream is removed from the holding tank and pumped to a centrifuge in the regeneration section where the precipitated MnO_2 is removed from the KNO_3 solution.

This KNO_3 solution is sent to an electrolytic cell to produce a weak HNO_3 solution (25-30%) and a mixed stream of KOH and KNO_3 . The final use of this HNO_3 stream is not specified but the mixed K salt stream is reacted with the earlier removed MnO_2 according to the following reaction:



The resulting potassium manganate (K_2MnO_4) is subjected to electrolytic reduction to regenerate KMnO_4 :



The regenerated K solution is pumped to the holding tank to be recycled to the absorber.

Status of Development

Initial testing of the Nissan Permanganate process was begun in the early 1970's. Since 1972 four small pilot plants (100-2000 Nm^3/hr) were constructed and operated treating the tail gas from HNO_3 plants.

This process has apparently not been tested on any type of power plant flue gas.

Since so little information is available for this process, it is difficult to project the next stage of development.

Background of Process Developer

Nissan Engineering, a subsidiary of Nissan Chemical Industries, Ltd., has developed this process using an alkali permanganate to convert the NO_x in HNO_3 tail gas to an alkali nitrate.

Nissan Engineering's experience in air pollution control is apparently limited to this process for HNO_3 tail gas with no background in treating power plant flue gas.

Published Economic Data

No information has been published on the total capital investment or the annual revenue requirements for the Nissan Permanganate process.

Raw Material, Energy, and Operation Requirements

No information about the raw material, energy, or operating requirements for this process has been published. The major raw material for the Nissan process would be makeup KMnO_4 and KOH . The major energy requirements would be electricity for both the electrolysis reactors and also operating the process equipment and fuel oil for the flue gas reheat section.

Technical Considerations

See similar section for MON Alkali Permanganate process.

Environmental Considerations

Essentially no information has been made available concerning the NO_x removal efficiency and the sensitivity of this removal efficiency to changes in either the flue gas composition or the operating conditions in the absorber.

The generation of a weak HNO_3 solution represents a significant waste disposal problem since there is essentially no market for this solution.

The generation of H_2 during the electrolytic oxidation of K_2MnO_4 represents a significant work hazard for this process due to its explosive nature.

Critical Data Gaps and Poorly Understood Phenomena

There is insufficient information available to discuss the critical data gaps in detail or to discuss the poorly understood phenomena. Hence, only the major gaps are included below.

1. Equipment operating conditions and sizes
2. MnO_4^- regeneration section
3. Stream flows and compositions
4. Estimated capital and operating costs
5. Raw material, energy, and operation requirements
6. Pilot plant data
7. Ability to handle power plant flue gas

Advantages and Disadvantages

Although sufficient information has not been published to enable a complete listing of the technical advantages and disadvantages for the Nissan Permanganate process, the following list has been compiled from the available data.

Advantages

None apparent at the present time.

Disadvantages

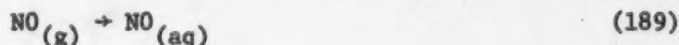
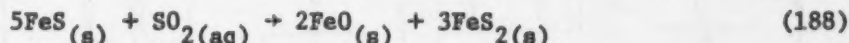
1. Forms secondary source of pollution (25% HNO_3)
2. Requires significant amounts of energy for the regeneration step
3. Has not been tested on coal-fired flue gas
4. Has not been developed beyond the conceptual design stage
5. Requires clean (SO_2 -free) gas feed
6. Uses significant amounts of stainless steel or exotic materials for process equipment
7. Requires flue gas reheat for plume buoyancy
8. Requires an expensive liquid-phase oxidant

PITTSBURGH ENVIRONMENTAL AND ENERGY SYSTEMS SCORE PROCESS - WET, ABSORPTION-REDUCTION (NO_x-SO_x)

Process Description and Principles of Operation (55, 76)

The Pittsburgh Environmental and Energy Systems' SCORE (SULF-X Concurrent Oxides Removal) process is a wet SO_x-NO_x removal process using a ferrous sulfide (FeS) solution to absorb both SO₂ and NO_x. This process is somewhat different from the other wet, absorption-reduction processes in that the sorbent material, FeS, is used to reduce both the SO₂ to elemental S and the NO_x to molecular N₂. The sorbent is then regenerated using carbon (C) as a reducing agent in a coal-fired kiln. The SCORE process consists of five major sections including (1) particulate removal (ESP), (2) absorption of SO₂ and NO_x, (3) separation and reduction of absorbent, (4) S recovery, and (5) ash-sludge disposal. A block flow diagram of this process is shown in Figure 26.

After passing through a cold ESP, the flue gas enters a quenching tower where a spray of recycle FeS slurry at a pH of 6 adiabatically humidifies and cools the flue gas from 150°C (300°F) to 53°C (127°F). In addition some of the SO₂ and NO_x are absorbed into the slurry in the quenching section and undergo the following reactions:



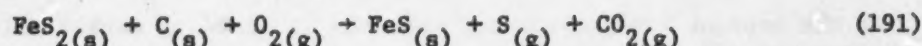
The liquid effluent from this section drops into a holding tank from which most of the slurry is recirculated.

The flue gas leaves the quench section and enters the first stage of the absorber where the gas passes cocurrently with a spray of makeup FeS slurry. The SO₂ and NO_x levels in the flue gas are further reduced by reactions (187) through (190). The slurry from this first stage of the absorber drops into the quench section holding tank to be recycled to the quench tower. The flue gas is further stripped of both SO₂ and NO_x in a second stage of the absorber by contacting a spray of regenerated FeS slurry. The flue gas from this second stage is passed through a mist eliminator, reheated, and exhausted through the stack.

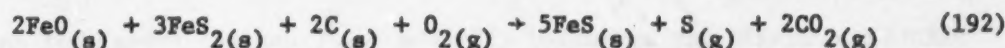
The spent slurry from the second stage of the absorber is pumped to a thickener where a purge stream of flyash and FeS is removed from the bottom

of the thickener. This bottom stream is sent to a filter where the solids are removed and purged from the system. The filtrate from this ash filter is combined with the thickener overflow and recycled to the absorber second stage after makeup H₂O has been added.

A purge stream from the quench tower holding tank is pumped to a thickener in the regeneration section. The thickener bottoms are filtered and sent to an indirectly fired regenerating kiln where coal is used both as a fuel for heating the kiln and as a source of C to reduce the ferrous disulfide (FeS₂) formed during the reduction of both the SO₂ and the NO. The primary reaction occurring in the kiln is:



The ferrous oxide (FeO) produced during the reduction of SO₂ and NO_x is also converted in this kiln according to the following reaction:



The off-gas from the reducing kiln is passed through a cyclone to remove some of the particulates and then is cooled to condense approximately 80% of the S as a liquid byproduct. The remaining gas is sent through the kiln firebox and then recycled to the flue gas duct to reenter the quench tower.

Recent tests are said (76) to indicate that the hot solids do not agglomerate and hence crushing equipment is no longer needed. Although not mentioned by the process developers, these hot solids (750°C) are probably cooled in a surge bin before being sent to a reslurrying tank. Feedstreams to the reslurrying tank include the thickener overflow and filtrate from the spent sorbent drying section. This regenerated FeS slurry is then recycled to the first stage of the absorber.

Status of Development

The SULF-X process was originally conceived in mid-1974 and in late 1974 bench-scale testing was begun. Although originally developed for flue gas desulfurization, early laboratory and subsequent field tests are said to have shown the capability of removing NO_x. After absorption tests were completed in March 1976, testing of the absorption section was begun in a 1-MW pilot plant treating flue gas from a coal-fired boiler at the U.S. Army's Fort Benjamin Harrison power plant. The regeneration of the spent sorbent, however, has not yet been demonstrated on a pilot-plant scale. During a 52-hr (2-day) continuous test of the absorption section, it was claimed that the SO₂ removal efficiency averaged 90% and the NO_x removal ranged from 60-70%. Pilot-plant testing was discontinued after only 2 mo of operation.

The next stage of development for this process would be to demonstrate long-term continuous operation with the entire system coupled as a unit in a small pilot-plant treating flue gas from a coal-fired boiler. At the present time plans are being finalized for such a pilot plant to be built at a Westinghouse plant in western Pennsylvania.

Background of Process Developer

Pittsburgh Environmental and Energy Systems, Inc. (PENSYS), is a small American company based in Pittsburgh with apparently very little previous experience in air pollution control. Most of their experience has been gathered during the development of their SCORs process, originally for FGD only, and later for simultaneous removal of SO₂ and NO_x.

At the present time no company has been licensed to market this technology and all inquiries about this process are handled by PENSYS offices in Pittsburgh.

Published Economic Data

PENSYS had originally estimated (55) the total capital investment and annual revenue requirements as \$12,500,000 and \$339,300, respectively, (assumed basis: U.S. and 1976 dollars) based on a 100-MW coal-fired boiler burning 3.5% S coal. The reported economics corresponds to a capital investment of \$125/kW of generating capacity and a revenue requirement of 0.49 mills/kWh. However, the regeneration system has recently been modified, as described in this report, and hence this economic data need to be updated. Although not specified by the process developer, the system was assumed to be able to remove 90% of the SO₂ and 60% of the NO_x from the flue gas containing approximately 1000 ppm SO₂ and 600 ppm NO_x.

Raw Material, Energy, and Operation Requirements (76)

The only major raw materials required for this process are FeS for makeup slurry and coal for the reducing kiln. PENSYS offers three or four sources of obtaining this FeS but the process vendors believe that the pyritic S from coal waste would be the most economical source. The following requirements have been estimated for a 100-MW coal-fired unit burning 3.5% S coal (2400 ppm SO₂ and 600 ppm NO_x) and assuming 90% of the SO₂ and 60% removal of the NO_x. (All quantities measured in tons are short tons.)

<u>Raw material</u>	<u>Quantity</u>
FeS	820 tons/yr
Coal	15,450 tons/yr

The major utility requirements include fuel oil for reheating the clean flue gas (which was not specified), electricity for operating the process equipment, and makeup H₂O. Although the process developers indicate recovered

heat from the regenerator could be used for reheating, without the installation of an additional ESP to sharply lower particulate emissions from the regenerator, it is uncertain whether this off-gas could be used as reheat. The quantities required, using the same basis as given above, would be:

Utility	Quantity
Electricity	1500 kW
Process water	265 gpm
Fuel oil (reheating)	Unknown

The operating manpower and maintenance requirements for this process (100 MW) have been estimated by PENSYS as two operators per shift and \$239,000/yr respectively.

Technical Considerations

The SCORE process developed by PENSYS appears to be a simple processing scheme that should be relatively easy to control. The process does not use a gas-phase oxidant and appears to be a simple scrubbing system with few pieces of equipment.

The NO_x removal efficiency is claimed to be relatively insensitive to inlet flue gas composition. In contrast with the other wet absorption-reduction processes, the sorbent in the scrubbing slurry is used to reduce both the SO_2 and the NO_x and hence no minimum amount of SO_2 in the flue gas is required. The SO_2 removal is also said to be insensitive to the inlet flue gas composition. The claim that this process is insensitive to the inlet particulate composition is not well understood since the combination of FeS solids and flyash in the scrubbing slurry would probably make the separation of the flyash difficult and lead to extensive losses of sorbent. Sensitivity to another important flue gas constituent, O_2 is not considered to be significant by the process vendors. However, it is well known that the Fe^{+2} ion, which is important in the absorption of NO_x , is readily oxidized to the Fe^{+3} ion by flue gas O_2 absorbed into the scrubbing solution. Although most of the Fe^{+2} ion is present in the slurry as a solid and hence practically immune to attack by flue gas O_2 , some will be present in the solution and will be oxidized to the Fe^{+3} ion.

The absorber uses cocurrent flow in each of the three stages for gas-liquid contact. The absorbent slurry is apparently pumped under pressure into the absorber and is sprayed downstream with the flow of the gas. The L/G ratio in the absorber is apparently very low, on the order of 10-15 gal/kaft³ of gas. The relative insolubility of NO , which makes up 90-95% of the total NO_x in the boiler flue gas, normally requires an L/G of 10-15 1/Nm³ (60-75 gal/kaft³) for reasonable NO_x removal. (See Technical Considerations under the other wet absorption-reduction processes.) The fact that the FeS is relatively insoluble in aqueous solution and hence not freely available for reducing both the SO_2 and the NO_x would seem to indicate that the L/G should be even higher than that for the other wet absorption-reduction processes for the same NO_x removal efficiency.

A major disadvantage of the PENSYS process is the extensive energy requirements in the regeneration section. The reducing kiln requires temperatures of about 750°C (1385°F) to regenerate the spent absorbent. Although some of this heat is recovered by recycling the S condenser off-gas to partially dry the incoming absorbent and preheat the air to the kiln, most of the energy expended in the kiln is apparently lost to the system. For example, the hot solids from the kiln are partially cooled in a surge bin and then H₂O quenched with none of this heat recovered.

Another potential problem concerns the purity of the byproduct S. Although a cyclone has recently been added to remove some of the particulate matter, the byproduct S from the PENSYS system may not be of the same quality as that produced in some of the other processes.

Since this is a wet simultaneous removal process, retrofitting this system on existing power plants should be relatively easy if sufficient land is available nearby for siting of the process equipment. The major modification to the existing plant would be the installation of a common plenum from the existing cold ESP to the four scrubber trains on a 500-MW boiler. This use of a common plenum and four absorber trains would allow this system to be easily turned down by simply closing off any combination of scrubber trains.

Although the process developers claim that most of the process piping and equipment can be made of carbon steel, for long-term operation the materials will have to be rubber-lined carbon steel to prevent the erosion and corrosion associated with circulating slurries and Cl⁻. The reducing kiln will probably have to be made of stainless steel due to both the high temperatures and the reducing atmosphere required to regenerate the spent sorbent.

Environmental Considerations

During a 52-hr test of the 1-MW pilot plant treating flue gas from a coal-fired boiler (1000 ppm SO₂ and 600 ppm NO_x), the absorption section of the SCORE process demonstrated 90% SO₂ removal and 60% NO_x removal. However, the data base on which the NO_x removal efficiency was determined is limited and hence further testing in the pilot plant is required to confirm the ability of this process to remove NO_x. The SO₂ is absorbed, reacted with the FeS in the scrubbing slurry, and regenerated to yield byproduct elemental S. The NO_x is absorbed, reduced by FeS, and exhausted as molecular N₂.

The only waste stream generated by this process is flyash-FeS sludge which will need to be purged to a landfill disposal site. The NO_x is reduced to molecular N₂ and hence no wastewater NO₃⁻ stream is generated. The SO₂ is recovered as elemental S and hence no waste limestone sludge is generated.

Critical Data Gaps and Poorly Understood Phenomena

The critical data gaps associated with the SCORE process developed by PENSYS include:

1. Size and operating conditions of process equipment
2. Stream compositions and flow rates
3. Long-term pilot plant data
4. Updated economic data including capital investment and revenue requirements

Included under poorly understood phenomena would be the following:

1. The ability of this process to achieve the claimed NO_x removal efficiencies does not seem reasonable under the operating conditions specified by the process developers.
2. The impact of the oxidation of the Fe^{+2} ion by flue gas O_2 on the absorption reactions and NO_x removal efficiency.
3. The process equipment and piping being constructed from mild carbon steel.
4. The low annual revenue requirements.
5. The recovery of marketable grade S with this process.

Advantages and Disadvantages

Since this is a wet simultaneous SO_2 - NO_x process, it has the following advantages and disadvantages as compared to the dry NO_x processes and the other wet processes.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Produces marketable byproduct (elemental S)
3. Has been tested on coal-fired flue gas on pilot-plant or greater scale
4. Operates with full particulate loadings ($>7 \text{ gr/sft}^3$)

Disadvantages

1. Can only achieve a maximum NO_x removal efficiency of $<70\%$
2. Requires significant amounts of energy for the regeneration step
3. Has not been operated as an integrated process
4. Has not been operated for a long-term continuous period
5. Incorporates questionable design features (absorber L/G appears to be too low for NO_x removal)
6. Uses significant amounts of stainless steel or exotic materials for process equipment
7. Requires hot solids handling
8. Requires flue gas reheat for plume buoyancy

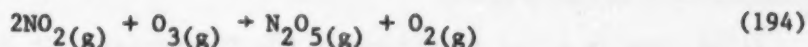
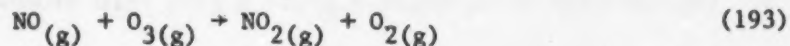
TOKYO ELECTRIC-MITSUBISHI HEAVY INDUSTRIES PROCESS - WET OXIDATION-ABSORPTION (NO_x)

Process Description and Principles of Operation (5)

The Tokyo Electric-Mitsubishi Heavy Industries (MHI) process is a wet oxidation-absorption system developed jointly by Tokyo Electric Power and MHI. This process was originally developed for treating clean flue gas (no SO_x) and for this reason would only be applicable for natural gas-fired boilers. The NO_x is oxidized by O₃ to N₂O₅, absorbed in H₂O to form 8-10% HNO₃, and concentrated to a 60% acid solution in the byproduct recovery section.

The Tokyo Electric-MHI system consists of four sections (1) gas-phase oxidation of NO_x, (2) absorption, (3) byproduct HNO₃ recovery, and (4) excess O₃ absorption. The overall outline of this process is shown in the block flow diagram in Figure 27.

The flue gas from the boiler is sent through a spray tower for adiabatic cooling and humidification and then injected with O₃ before entering an oxidizing tower. The NO_x is rapidly and selectively converted to N₂O₅ by the following reactions.



The flue gas from the oxidizing tower passes countercurrently to a weak aqueous HNO₃ solution in a packed absorption tower. The liquid from the bottom drops into an absorber holding tank while the clean flue gas flows to a second packed tower. In this second absorber the flue gas passes countercurrently to a CaSO₃·1/2H₂O slurry to remove any remaining O₃ prior to reheating and eliminating the flue gas.

The dilute aqueous solution from the NO_x absorber holding tank is recirculated through the NO_x absorber after makeup H₂O has been added and a small purge stream has been removed. This purge stream is pumped to a storage tank in the byproduct recovery section. The aqueous HNO₃ solution is apparently pumped to a steam evaporator where the acid is concentrated from about 10 to 60% and then stored and sold in this form.

The CaSO₃·1/2H₂O slurry from the O₃ removal absorber drops to a holding tank from which most of the slurry is recycled after makeup CaSO₃·1/2H₂O has been added. A small purge stream is removed and pumped to a waste disposal pond.

Status of Development

Initial testing of the Tokyo Electric-MHI process was conducted from December 1973 to September 1974 in a small pilot plant at the Minamiyokohama power station of Tokyo Electric. This pilot plant treated 2000 Nm³/hr

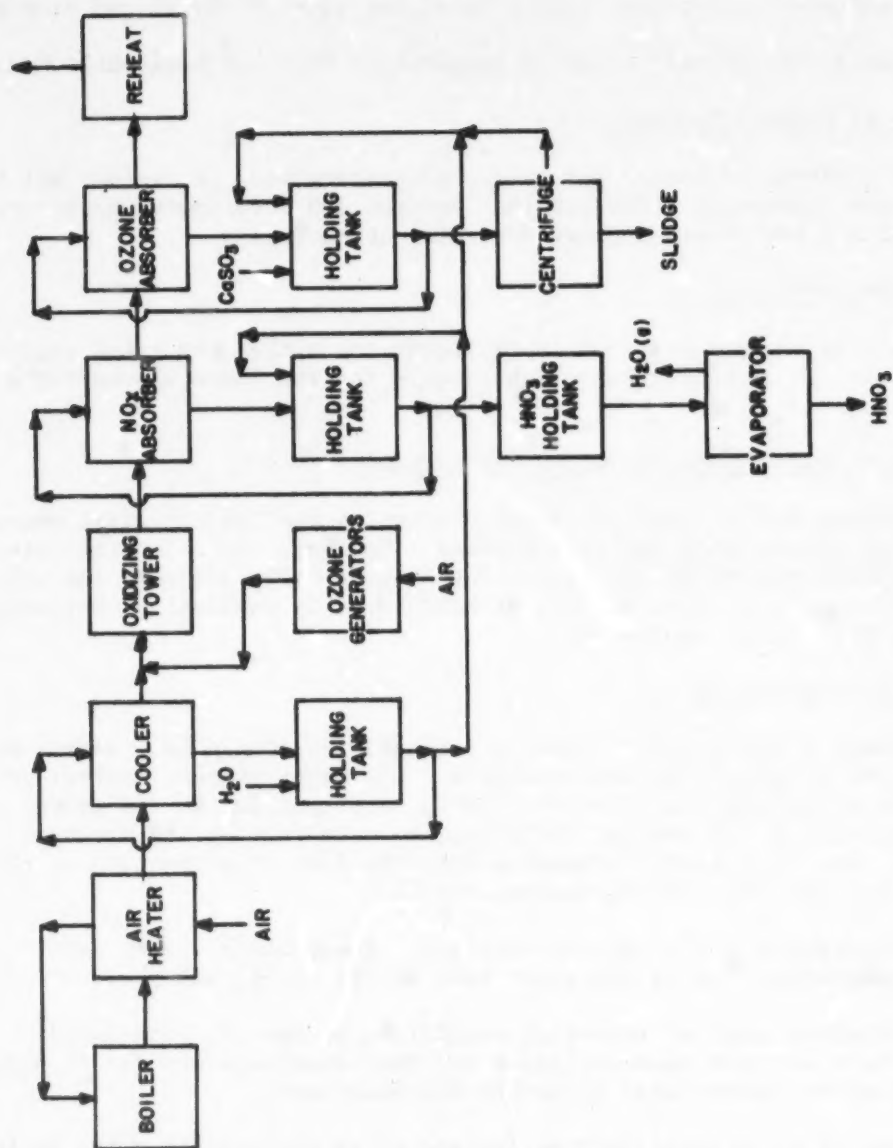


Figure 27. Flow Diagram of Tokyo Electric-Mitsubishi Heavy Industries Process.

(0.6 MW equiv) of flue gas from a gas-fired boiler containing 90-220 ppm NO_x . More than 90% NO_x removal was achieved. Other operating conditions and results have not been made available.

In December 1974 a prototype unit at the same power plant began operating based on the same technology. This unit treated 100,000 Nm^3/hr (33.3 MW equiv) of flue gas from the gas-fired boiler. Operating conditions and results of this prototype testing have not been published.

This process has not been tested on either oil- or coal-fired flue gas.

The plans for the next stage of development have not been published.

Background of Process Developer

Tokyo Electric is one of the larger power companies in Japan. MHI has had extensive experience including the research and development of several FGD systems and two other flue gas denitrification systems.

Published Economic Data

No information has been published concerning either the total capital investment or the annual revenue requirements for the Tokyo Electric-MHI process.

Raw Material, Energy, and Operation Requirements

No information has been published concerning the raw material, energy, or operating requirements for this process. However, the major raw material for the Tokyo Electric-MHI system would be makeup $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$. The major energy source would be electricity, primarily for O_3 generation, but also to operate the process equipment.

Technical Considerations

The Tokyo Electric-MHI process is a relatively simple NO_x removal process with few pieces of process equipment. The major process control problem will be generating and injecting the O_3 in proportion to the amount of NO_x passing through the system. Although not mentioned by the process developers, the O_3 is probably metered into the duct in proportion to the measured flue gas rate and NO_x concentration.

The NO_x removal efficiency is relatively insensitive to the inlet flue gas composition and is dependent only on the $\text{O}_3:\text{NO}_x$ mol ratio.

The relative size and operating conditions in the two packed-bed absorbers have not been made available but they should be similar in size and operation to conventional limestone FGD absorbers.

The use of O_3 to generate N_2O_5 instead of simply oxidizing the NO to NO_2 will result in at least a 50% increase in the consumption of O_3 (typically $\text{O}_3:\text{NO}_x$ mol ratio of 1.7) over that required for the wet simultaneous

SO₂-NO_x processes using O₃. Since the cost of O₃ generation typically represents approximately 30-40% of both the total capital investment and annual revenue requirements for the flue gas denitrification system, increasing the O₃ consumption by more than 50% would seem to rule out the widespread use of this process due to economic considerations.

This high mol ratio of O₃:NO_x results in the need for a second absorber to remove any remaining O₃ before releasing the flue gas through the stack. A circulating CaSO₃·1/2H₂O slurry containing a proprietary catalyst is used to absorb this O₃ and generate a byproduct sludge containing both SO₃²⁻ and SO₄²⁻ salts of Ca. This byproduct sludge would be pumped to a waste disposal pond.

Further diminishing the usefulness of this process in the U.S. power industry is the fact that it can be used only on clean flue gas, i.e., SO_x free. Although the process developers have not listed specific reasons for requiring SO₂-free flue gas, it would apparently complicate the chemistry of the acid solution and prevent the removal of pure HNO₃ as a byproduct.

Retrofitting this system on power plants would be relatively easy providing sufficient land was available adjacent to the power plant for siting the process equipment. The installation of a common plenum to interconnect the four scrubber trains on a 500-MW boiler would also be required. With the use of four trains, the NO_x removal system could easily cycle with the availability of the boiler.

The primary material used in the construction of the process equipment and piping would be 304L stainless steel. The only exceptions would be the oxidizer which will be plastic-lined stainless steel.

Environmental Considerations

During the operation of the prototype unit (33 MW equiv) at Minamiyokohama power station treating flue gas from a gas-fired boiler (100-200 ppm NO_x), this process was able to maintain better than 90% NO_x removal. The NO_x is absorbed and removed as a weak HNO₃ solution.

The Tokyo Electric-MHI process is designed specifically for NO_x removal and does not remove any other pollutants.

The NO_x removal efficiency is dependent on the amount of O₃ injected. If the mol ratio of O₃:NO_x in the flue gas declines below 1.7, the acid bleed stream will contain a mixture of HNO₂ and HNO₃. The percentage of acid stream present as undesirable HNO₂ will increase as the O₃:NO_x ratio decreases until an equimolar mixture of HNO₂ and HNO₃ is reached at an O₃:NO_x ratio of (1.0-1.1):1. As the O₃:NO_x mol ratio drops below 1.1, the NO_x removal efficiency will decrease below 90%. A complete failure of the O₃ generation equipment will result in an NO_x removal efficiency of approximately 5%.

The use of O₃ presents a significant work hazard since it is a strong oxidizing agent even at low concentrations.

Critical Data Gaps and Poorly Understood Phenomena

Included under critical data gaps are the following:

1. Stream flows and compositions
2. Absorber operating conditions
3. Economic data
4. Pilot or prototype data and results
5. Nature and cost of oxidation catalyst
6. Maintenance and manpower requirements

Poorly understood phenomena would include the reason why this process can only be used to treat clean flue gas.

Advantages and Disadvantages

The primary advantage of the Tokyo Electric-MHI wet oxidation-absorption process is its high NO_x removal while the major disadvantage is the high consumption and hence cost of O_3 . Other advantages and disadvantages are listed below.

Advantages

1. Achieves >90% NO_x removal efficiency
2. Produces a potentially marketable byproduct (60% HNO_3)

Disadvantages

1. Requires significant amounts of energy for the regeneration step
2. Has not been tested on coal-fired flue gas
3. Requires clean (SO_2 - and particulate-free) gas feed
4. Uses significant amounts of stainless steel or exotic materials for process equipment
5. Requires flue gas reheat for plume buoyancy
6. Requires an expensive gas-phase oxidant

UBE INDUSTRIES PROCESS - WET OXIDATION-ABSORPTION (NO_x)

Process Description and Principles of Operation (5)

The Ube Industries wet NO_x removal process was originally developed to treat the tail gas from HNO₃ plants. The absorption of NO_x is based on the injection of an NO₂-rich stream to obtain an equimolar NO:NO₂ ratio in the flue gas. Although this system may be feasible for an HNO₃ plant, its ability to treat power plant stack gas is highly questionable primarily because there is no source of NO₂-rich gas readily available at a power plant. Since Ube has not suggested any modified method for treating flue gas, this process will not be evaluated further.

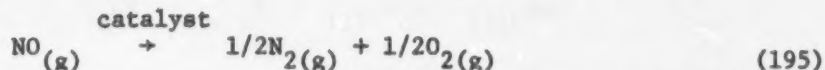
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DRY NO_x REMOVAL PROCESSES

INTRODUCTION TO THE DRY FLUE GAS DENITRIFICATION PROCESSES

Various dry flue gas denitrification methods have been developed because of the need for integration of NO_x removal with existing SO₂ removal systems and the high cost and the adverse environmental consequences from the liquid and solid waste products of wet denitrification processes. The major modes of dry NO_x removal which have been studied include (1) catalytic decomposition, (2) selective catalytic reduction (SCR), (3) nonselective catalytic reduction, (4) selective noncatalytic reduction, (5) adsorption, and (6) electron beam radiation.

Catalytic decomposition would appear to be the most attractive means of eliminating NO_x from flue gas. By this method, NO (90-95% of the total NO_x) is converted to N₂ and O₂ in the presence of a catalyst as follows:



Unfortunately, the reaction rates and NO removal efficiency have been quite low on tests performed to date with known catalysts. Thus, this method is generally considered impractical at present for flue gas denitrification (1, 2, 34, 72) and therefore has not been included in this study.

One of the most promising means of NO_x removal for combustion flue gas involves SCR. This process uses NH₃ to selectively reduce NO_x to N₂ and H₂O in the presence of a catalyst.

Another catalytic reduction process consists of nonselective NO_x reduction. The major reductants used are hydrocarbons (such as CH₄), CO, and H₂. In this system ample reductant must be used to reduce all the oxidant components of the flue gas, which for a typical coal-fired flue gas are primarily O₂, SO_x, and NO_x.

Selective noncatalytic reduction of NO_x incorporates a gas-phase homogeneous reaction of a selective reductant (such as NH₃) converting NO_x to N₂. This mode of NO_x removal differs from SCR in that much higher temperatures are used and the need for a catalyst is obviated.

NO_x adsorption has been studied in two different areas. For HNO₃ plant tail gas, which is free of SO_x and large quantities of H₂O, NO_x may be adsorbed by molecular sieves, gelatinous silica, etc. The adsorbed NO_x is then released by heating and returned to the acid plant. This method,

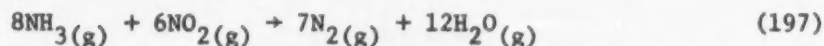
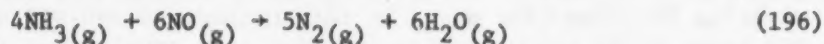
however, is generally not applicable for combustion flue gas containing SO_x , H_2O , and dust; therefore, processes of this type are not included in this study. Another process using a special activated char (developed for SO_x removal) is suitable for NO_x removal from combustion flue gas containing some particulates. The adsorbed NO_x is converted to N_2 in a high-temperature char-regeneration vessel. One process of this type is included in this report.

A completely novel process for simultaneous SO_2 - NO_x removal from flue gas incorporates flue gas bombardment with electron beam radiation.

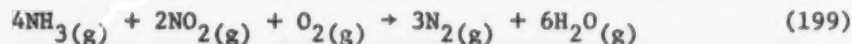
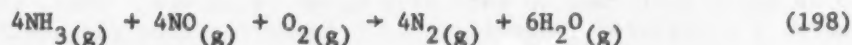
Each of these types of dry NO_x removal processes with the exception of the catalytic decomposition type is discussed in the following section. Table 16 summarizes a comparison of the different types of NO_x removal. Also, each of the denitrification processes included in this study is listed by type in the following section. A detailed explanation of each of these dry processes is presented in the final portion of this chapter.

SCR

The SCR processes take advantage of the reduction selectivity of NH_3 for NO_x . The reactions of NH_3 with NO_x are usually given in the process descriptions as follows:



In most instances, however, the reactions may be better represented according to the following:



The above may more accurately express the reactions because several studies have demonstrated that the presence of at least some O_2 improves the NO_x reduction (2, 26, 34, 72, 84).

There are primarily two basic classifications of catalyst used: metal and C based. The metal catalyst may be subdivided into noble and nonnoble metal catalysts. Much development has been completed on both the noble and nonnoble catalysts, but the noble catalysts are generally considered impractical for the selective reduction of NO_x with flue gas containing SO_x (72, 88). The noble catalysts are easily poisoned by S compounds and are more expensive. Nonnoble metal oxides are the catalysts used in most of the processes reported herein. Although less efficient and requiring higher temperatures (300-400°C) than noble catalysts, they are less expensive, more resistant to SO_x poisoning, and do not promote N_2O production as has been reported for some noble catalysts (88).

TABLE 16. COMPARISON OF DRY NO_x REMOVAL PROCESSES

Process characteristics ^a	Dry NO _x removal process type				
	Selective catalytic reduction	Nonselective catalytic reduction	Selective noncatalytic reduction	Adsorption	Radiation
Simultaneous SO ₂ -NO _x removal	- ^b	X	-	X	X
Achieves moderate SO ₂ removal (>85%)	-	X	-	X	X
Achieves high NO _x removal (>90%)	X	X	-	-	X
Operating conditions	-	-	-	X	X
Produces waste stream	X	-	X	-	-
Uses NH ₃	X	-	X	-	-
Forms NH ₄ HSO ₄	X	-	X	-	-
Operates with sensitivity to particulates	X	-	X	X	-
Produces marketable byproduct	- ^b	X	-	X	-
Current development status	- ^b	-	-	X	-
Tested on coal-fired flue gas	- ^b	-	-	-	-
Tested on pilot plant or larger scale	X	-	X	X	X

a. An "X" indicates the process has this characteristic.

b. Depends on process.

The C-based catalysts are used for simultaneous NO_x and SO₂ removal. C is used commercially as an SO₂ adsorbent and activated C's have been developed with special structures or metallic constituents for aiding the NO_x and NH₃ reduction reaction. Operating temperatures, averaging 200-250°C with these C-based catalysts, are usually lower than the operating temperatures with the base-metal catalysts. The lower temperatures provide increased SO₂ adsorbing capability, though higher temperatures favor greater NO_x removal efficiency.

Several problems are associated with the use of SCR processes in combustion flue gases. As already mentioned concerning noble catalysts, SO_x poisoning of the catalyst is a problem. SO_x usually attacks the catalyst carrier. For example, SO_x, especially SO₃, tends to react with Al₂O₃ to form an Al₂(SO₄)₃, thus, decreasing the available surface area and catalyst activity. Base-metal oxide catalysts also react with SO_x to varying extents; however, these base-metal sulfates are still reactive.

Other problems are the decrease in catalyst activity and the increase in pressure drop which are created from particulate pluggage of the reactor. Methods used to minimize these problems are parallel passage reactors, moving-bed reactors, regeneration steps, and specially shaped catalysts.

The formation of NH₄HSO₄ presents another concern with the use of SCR processes. It is usually formed downstream from the reduction reactor as the flue gases are cooled in heat exchange equipment according to the following reaction:



The conditions at which it is formed are shown in Figure 28. For example, NH₄HSO₄ would form at 210°C or below with 10 ppm each of SO₃ and NH₃. NH₄HSO₄ is corrosive and also interferes with heat transfer in the heat exchange equipment. At even lower temperatures it may solidify and form NH₄HSO₄. When these products do form, occasional steam blowing or washing out with H₂O are needed for their removal.

Another important factor which must be considered is the availability and cost of NH₃ for NO_x reduction systems. It has been estimated, based on a 100 ppm NO_x regulation for a coal-fired boiler in 1985, that a 30-50% increase in NH₃ production capacity in the U.S. may be necessary for utility boilers alone (108). This large increase in production demand and future cost increases for NH₃ will significantly affect the NH₃ availability and economics for NO_x removal technologies using NH₃.

The companies which have investigated or are developing SCR processes which are included in this report using metal or similar catalysts are the Enviro-nics, Inc. - Enecon Corporation; Exxon Research and Engineering Company; Hitachi, Ltd.; Hitachi Zosen; JGC Corporation; Kobe Steel, Ltd.; Kurabo Industries, Ltd.; Mitsubishi Kakoki Kaisha, Ltd.; Mitsubishi Heavy Industries, Ltd.; Mitsubishi Petrochemical Company, Ltd. (only catalysts are offered); Mitsui Engineering and Shipbuilding Company; Mitsui Toatsu

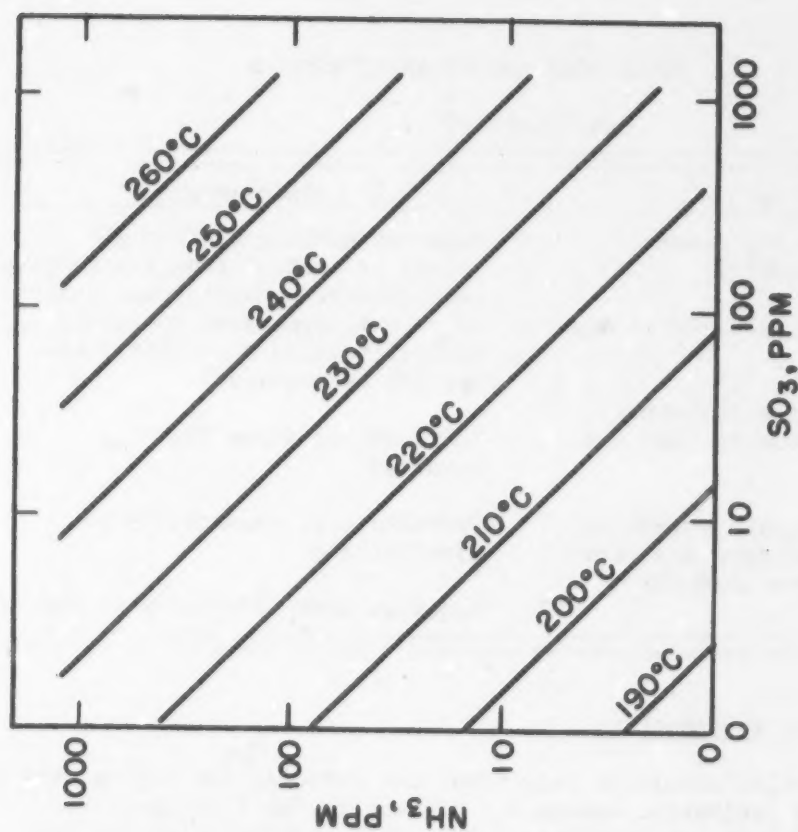


Figure 28. Temperatures Below Which NH_4HSO_4 Forms (101).

Chemicals, Inc.; Sumitomo Chemical Company, Inc.; Sumitomo Heavy Industries, Ltd. (NO_x-only removal process); Ube Industries, Ltd.; and Universal Oil Products (both the simultaneous NO_x-SO₂ removal and the NO_x-only removal processes). Other companies with SCR processes which are not described in this report include Asahi Glass Company (2) (no information obtained) and Nippon Kokan (13, 14). (Personal communications with Nippon Kokan indicated development was just beginning with no information presently available for release.) Companies developing SCR processes incorporating C-based catalysts are Sumitomo Heavy Industries, Ltd.; Takeda Chemical Industries, Ltd.; and Unitika, Ltd.

General advantages and disadvantages for SCR processes are indicated in Table 17. A summary description of each of the SCR processes is listed in Table 18.

TABLE 17. ADVANTAGES AND DISADVANTAGES OF
SCR PROCESSES

Advantage	Disadvantage
Achieves excellent NO _x removal (usually 90% or greater)	Requires heating of flue gas to attain or control reaction temperature (however, development underway on several processes to locate denitrification such that reheat may not be required)
Creates no waste byproducts in most processes	Emits NH ₃ or forms NH ₄ HSO ₄ , possibly
Demands lower capital investment and revenue requirements than wet processes	Operates with sensitivity to particulates
Uses gas-phase reaction chemistry and, therefore, requires less complex operation steps than wet processes	Requires some difficulty to retrofit

Nonselective Catalytic Reduction

With nonselective catalytic reduction, the reducing gas reacts with the oxidant components (primarily excess O₂) present in the flue gas. For a typical coal-fired flue gas, sufficient reductant must be added for the reduction of O₂, SO_x, and NO_x. Hydrocarbons, (i.e., CH₄), CO, and H₂ are the major reductants used. A typical overall reaction using CO as the reductant is as follows:



TABLE 18. PROCESS CONDITIONS AND ECONOMICS
FOR DRY SCR NO_x REMOVAL PROCESSES

Company	Development status (MW equiv)	Removal efficiency, %		Catalyst	Reaction temp., °C	Space velocity, hr ⁻¹	Mol NH ₃ per mol NO _x	By-products	Reported capital investment, \$/kW ^a	Reported revenue requirement, mills/kWh ^a
		NO _x	SO ₂							
Eneron	Pilot (1.5)	65 (oil) 85 (gas)	- ^b	0.03% Pt by wt	280-305 235	35,000 30,000	2.0-2.5	None	11 ^c	0.2 ^c
Exxon ^d	Bench (0.003)	70-95	90-95	-	315-370	2,000-5,000	0.7-1.0	None	-	-
Hitachi Ltd.	Comm (170)	>90	- ^b	-	300-400	10,000-20,000	0.9-1.1	None	45	-
Hitachi Zosen	Comm ^e (275)	>90	- ^b	-	300-400	4,000-6,000 ^f	0.8-1.2	None	16	1.5
JGC Corp.	Proto (23)	>95	- ^b	-	380-420	-	1.1-1.3	None	27	-
Kobe	Bench (0.3)	90	- ^b	Base metal	350-400	10,000	1.0-1.1	None	12-21	1.3-1.7
Kurabo	Proto (10)	>90	- ^b	CuO ^g	350-400	7,000-10,000	0.9-1.0	None	35	1.4
Kureha	Pilot (1.6)	90	- ^b	-	150	5,000	1	None	-	-
Mitsubishi Heavy Ind.	Pilot (1.3)	90	- ^b	-	350-400	4,000-10,000 ^h	1	None	-	-
Mitsubishi EX	Pilot (4.7)	>90	- ^b	Fe ₂ O ₃ ·H ₂ O	400-450	3,000-5,000	1.0-1.3	None	36	1.8
Mitsubishi Petro. ⁱ	-	95	- ^b	Titanate	300-600	10,000	1	None	- ^b	- ^b
Mitsui E & S	Comm (67)	90	- ^b	Base metal	350	5,000	1	None	10	-
Mitsui Toatsu	Proto (30)	>90	- ^b	-	350-400	3,000-10,000	1.0-1.2	None	49	1.6
Sumitomo Chemical	Comm (100)	90	- ^b	Base metal	300-350	10,000	1	None	80 ^j	1.2 ^j
Sumitomo Heavy Ind.	Bench (0.5)	>90	- ^b	Metal oxide	270-370	5,000	1	None	30	2.3
Sumitomo Heavy Ind.	Pilot (3.3)	85-90	95	Act. carbon	200-230	1,000-1,700	2.0-2.5	H ₂ SO ₄	46	5.9
Takeda	Pilot (3.3)	90	80	Act. carbon	210-230	1,000-3,000	0.7-1.2 ^k	- ^l	90	0.65
Tobe	Pilot (3.3)	90	- ^b	-	350-400	10,000	1.1-1.3	None	-	-
Unitika	Bench (0.07)	>90	- ^b	-	320-410	10,000-15,000	1.0-1.1	-	24	2.1
Unitika	Pilot (1.5)	>90	>90	Act. carbon	200-250	1,000	- ^m	H ₂ SO ₄	60	6.8
UOP	Proto ⁿ (40)	>80	90	CuO/CuSO ₄	400	7,000-10,000	1.0-1.2	-	131 ^o	5.0 ^o
UOP	Proto ^p (40)	>90	- ^b	CuSO ₄	400	4,000-8,000	1.0-1.2	None	31 ^o	1.4 ^o

a. Unless otherwise noted, cost based on 1976 dollars and Japanese location; see each detailed process description for additional bases.

b. Not applicable.

c. Based on 1975 cost and U.S. location.

d. Exxon has studied both simultaneous NO_x-SO₂ removal and NO_x-only removal.

e. Being tested on 0.07-MW equiv coal-fired unit.

f. Area velocity is more appropriate terminology and is 7-10 Nm³/hr/m²; with a catalyst surface area to volume ratio of 550-660 m²/m³, a S.V. of about 4,000-6,000/hr is obtained.

g. Kurabo has newly developed iron-based catalyst which is more suitable for coal-fired flue gas.

h. Based on intermittent moving catalyst bed on semidirty gas; S.V. is 1,600-2,300/hr for parallel passage reactor with dirty gas.

i. Offering catalyst only.

j. Capital investment is based on treatment of dirty gas using an ESP. The revenue requirement is in 1973 dollars and based on treatment of clean gas at the Higashi Nihon Methanol plant.

k. This is mol NH₃/mol (NO_x + SO₂).

l. CaSO₄ and NH₃ is produced with washing method of regeneration; H₂SO₄ is produced with heating method of regeneration.

m. Moles NH₃ = (0.8) moles NO + (0.3-0.5) moles SO_x.

n. UOP has performed tests with coal-fired flue gas on 0.6-MW equiv pilot plant in FGD mode.

o. These costs are based on 1977 dollars and U.S. locations.

p. NO_x-only removal has been tested at the same 40-MW equiv treatment facility which normally operates with simultaneous SO_x and NO_x removal.

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Most of the development work in this area has been done on HNO_3 plant tail gas and the exhaust from internal combustion engines. Catalysts for these cases are inappropriate for power plant use and nonnoble metal catalysts which are efficient may require operating temperatures of at least 500°C (930°F) (72). A number of nonselective reduction catalysts promote the formation of H_2S and carbonyl sulfide (COS) which are toxic. If CO is used as the reductant, toxic metal carbonyls may be formed by the reaction of CO with the active metal portion of the catalyst, walls of the reactor, or trace metals in the flue gas. Of course, there is also the potential problem of unreacted CO emissions.

The only nonselective catalytic reduction process contained within this report is the Ralph M. Parsons Company process. Table 19 shows the general advantages and disadvantages of nonselective catalytic reduction systems. Process operating conditions and economics for The Ralph M. Parsons process are included in Table 20.

TABLE 19. ADVANTAGES AND DISADVANTAGES OF
NONSELECTIVE CATALYTIC REDUCTION PROCESSES

Advantage	Disadvantage
Removes NO_x and SO_x	Uses large amount of reductant to reduce all oxidants in the flue gas (O_2 , SO_x , NO_x)
Produces S as a byproduct	
Creates no waste byproducts	Requires greater development than other methods
Demands lower capital investment and revenue requirements than wet processes	Increases potential for toxic gas formation in flue gas
Uses gas-phase reaction chemistry and, therefore, requires less complex operation steps than wet processes	Increases potential for corrosion
	Requires reheat
	Operates with sensitivity to particulates
	Requires some difficulty to retrofit

Selective Noncatalytic Reduction

The selective noncatalytic reduction method simply combines a reductant (for example, NH_3) with the NO_x in a flue gas at the appropriate temperature without any catalyst to convert the NO to N_2 and H_2O . Though a complex-free radical chain mechanism is involved, the overall reaction may be simply expressed as follows:

TABLE 20. PROCESS CONDITIONS AND ECONOMICS FOR DRY NO_x REMOVAL PROCESSES OTHER THAN SCR TYPE

Item	Process type (company)			
	Nonselective catalytic reduction (Ralph M. Parsons)	Selective noncatalytic reduction (Exxon)	Adsorption (Foster Wheeler)	Radiation (Ebara-JAERI)
Development status	Not tested	Commercial	Prototype	Pilot plant
Size, MW equiv	-	53	20	1.0
NO _x removal, %	-	60-70	40-60	90
SO ₂ removal, %	-	- ^a	80-95	80
Catalyst or adsorbent	- ^b	None	C	None
Reaction temperature, °C	-	705-760	120-150	110
Space velocity, hr ⁻¹	-	- ^a	- ^a	- ^a
NH ₃ :NO _x mol ratio	- ^a	3.0-4.0	- ^a	- ^a
Byproducts	S	None	S	- ^c
Reported capital investment, \$/kW	21.7 ^d	-	40-90 ^e	1,000 ^f
Reported revenue requirement, mills/kWh	1.0 ^d	0.6-1.4 ^g	1.0-2.3 ^e	-

a. Not applicable.

b. Proprietary.

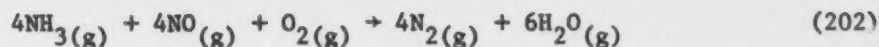
c. Multicomponent material, composition unknown.

d. Based on 1972 dollars and U.S. location.

e. Based on 0.9-4.3% S in fuel and 1977 dollars with U.S. location.

f. Based on 1976 dollars and Japanese location.

g. Based on \$0.07-\$0.15/MBtu; assumed 9,000 Btu/kWh heat rate for coal; 1976 costs with U.S. location.



NH_3 and O_2 also combine with each other to form NO but, at the required temperature, reaction (202) is favored and substantial NO reduction can be achieved. The optimum temperature needed when only NH_3 is added is about 1000°C ($\approx 1850^\circ\text{F}$) but the optimum temperature is reduced to about 730°C (1350°F) by injecting H_2 , either simultaneously with NH_3 or just downstream of the NH_3 introduction site.

One of the problems with this method is that the favorable temperature range is very narrow for optimum NO_x reduction. In power plant operations with a varying load and subsequent flue gas temperature changes, the $\text{NH}_3:\text{H}_2$ ratio must be corrected to match the changing temperature. If an imbalance between $\text{NH}_3:\text{H}_2$ ratio and flue gas temperature exists, either of two adverse consequences may result. If the temperature is too high, NH_3 will be converted to form additional NO . If the temperature is too low, unreacted NH_3 and NO may exit in the flue gas. The use of H_2 may present problems for power plant utilization either in the purchasing or generating of H_2 . The safety aspect of applying H_2 in a power plant must be considered, also. The potential for NH_4HSO_4 formation is relevant here as in SCR processes. Also, the future NH_3 availability and cost are very significant aspects which must be considered as mentioned under the SCR section.

Exxon's Thermal Denox process is incorporated in the detailed section of this report as a selective noncatalytic reduction method. The general advantages and disadvantages of selective noncatalytic reduction are given in Table 21. Process operating conditions and economics for Exxon's Thermal Denox system are shown in Table 20.

TABLE 21. ADVANTAGES AND DISADVANTAGES OF
SELECTIVE NONCATALYTIC REDUCTION PROCESSES

Advantage	Disadvantage
Requires no reheat	Achieves only about 60-70% NO_x removal
Requires no catalyst	Needs large amount of reductant (NH_3); $\text{NH}_3:\text{NO}_x$ mol ratio $>3:1$
Demands one of the least capital investments of any NO_x removal method	Operates with narrow optimum temperature range with potential for emission of NH_3 and NO during boiler load variations
Creates no waste byproducts	
Uses homogeneous, gas-phase reaction and, thus, requires least complicated operation steps of any process	

Adsorption

A system was developed using a special activated char with exceptionally good SO₂ adsorption capability. In pilot-plant tests, it was detected that this system also removed NO_x. The NO_x is adsorbed in the char, though the mechanism is still unknown. The adsorbed NO_x is changed to N₂ as the char is subjected to a temperature of about 650°C (1200°F) in a regeneration vessel. The N₂ exiting the regeneration section eventually reenters the adsorber and passes through to the stack. The major problem with this system is the low NO_x removal capability (about 40-60%).

Bergbau-Forschung and the Foster Wheeler Energy Corporation developed this system. The general advantages and disadvantages are listed in Table 22, while Table 20 lists the process operating conditions and economics for the Foster Wheeler process.

TABLE 22. ADVANTAGES AND DISADVANTAGES OF ADSORPTION PROCESS

Advantage	Disadvantage
Removes NO _x and SO _x	Obtains only 40-60% NO _x removal
Requires no reheat	Requires waste disposal of ash
Produces S as a byproduct	Uses more complex operation steps than other dry processes
Demands lower capital investment and revenue requirements than most wet processes	Requires hot solids handling

Electron Beam Radiation

A newly developed method of NO_x removal involves treating the flue gas with electron beam radiation. NO_x and SO_x are both removed and a byproduct comprised of S, N, O, and H with unknown chemical composition is formed. The major drawbacks at present are the high cost and waste product handling.

This method is included in this report under the Ebara Manufacturing Company and Japan Atomic Energy Research Institute (Ebara-JAERI) process. The advantages and disadvantages are displayed in Table 23. Table 20 includes a summary description of the Ebara-JAERI process.

TABLE 23. ADVANTAGES AND DISADVANTAGES OF RADIATION PROCESS

Advantage	Disadvantage
Removes NO _x and SO _x (may achieve >90% NO _x removal)	Demands large capital investment
Requires only electricity	Needs development of waste product treatment
Uses less complex operation steps than wet processes	

EBARA-JAERI PROCESS - DRY, ELECTRON BEAM RADIATION (NO_x - SO_x)

Process Description and Principles of Operation (2, 4, 5, 83, 105)

Ebara Manufacturing Company and Japan Atomic Energy Research Institute (JAERI--a government organization) jointly developed an electron beam radiation process for simultaneously removing SO_2 and NO_x from flue gas. A flow diagram of the process for a commercial power plant based on the process flow used in bench-scale tests is shown in Figure 29. The flue gas from a boiler, after passing through the air heater, passes through a highly efficient ESP for particulate removal. The gas is discharged from the ESP to the reactor where it is bombarded with an electron beam. Within the reactor, a powder comprising S, N, O, and H, and an H_2SO_4 mist are generated. After exiting the reactor, these byproducts are removed from the flue gas by passage through another ESP and then the byproducts are treated. (This treatment of byproduct is included here as necessary for commercial operation; however, it has not been tested at the pilot plant.) The gas continues to the stack. During bench-scale tests a recycle stream is taken from the reactor exit, passes through an ESP for removal of the byproduct formed in the reactor, and is reintroduced into the reactor. For a commercial plant, it would be more practical to pass all the gas exiting the reactor through one ESP and then take the recycle stream at the exit of this ESP and send it back to the entrance of the reactor. This would eliminate one ESP.

As shown in Figure 30, at 110°C (230°F) and employing a flue gas containing 80 ppm NO_x and 600-900 ppm SO_2 , an electron beam of 0.8 Mrad (radiation for 2 sec at an intensity of 0.431 Mrad/sec) removes 90% of the NO_x . An SO_2 removal of 80% is obtained with a 4 Mrad electron beam (radiation for 10 sec at the same intensity). A lower temperature allowed radiation to slightly increase the removal efficiency. The most probable radiation rate is in the 10^5 - 10^8 rad/sec range. The total rate is preferably between 10^6 - 10^7 rad. The residence time of the gas in the reactor may vary from 1-20 sec.

Various means of utilizing the byproduct formed in this NO_x and SO_2 removal process have been studied on small laboratory-scale experiments. In one method, the byproduct is heated to 90 - 120°C (194 - 248°F) to create an anhydrous substance. This anhydrous material is decomposed to NO_x and a denitrogenated anhydrous material at 160 - 240°C (320 - 464°F) in the presence of an inert gas (and/or N_2) and in the absence of O_2 . The NO_x is then converted to NO_2 in the presence of air at less than 140°C (284°F) and the NO_2 is used for HNO_3 production. SO_2 is produced by heating the denitrogenated anhydrous material to 240 - 270°C (464 - 518°F) in the presence of an inert gas. This SO_2 may be used to form H_2SO_4 .

A variation of the above process for handling the byproduct includes heating the material to 165 - 240°C (329 - 464°F) in the presence of an inert gas (excluding the use of N_2). N_2 , O_2 , and a denitrogenated material results from the above operation. The N_2 and O_2 are released to the atmosphere. The remaining substance is thermally decomposed to form SO_2 at 240 - 270°C (464 - 518°F) in the presence of an inert gas and the SO_2 is used to produce H_2SO_4 .

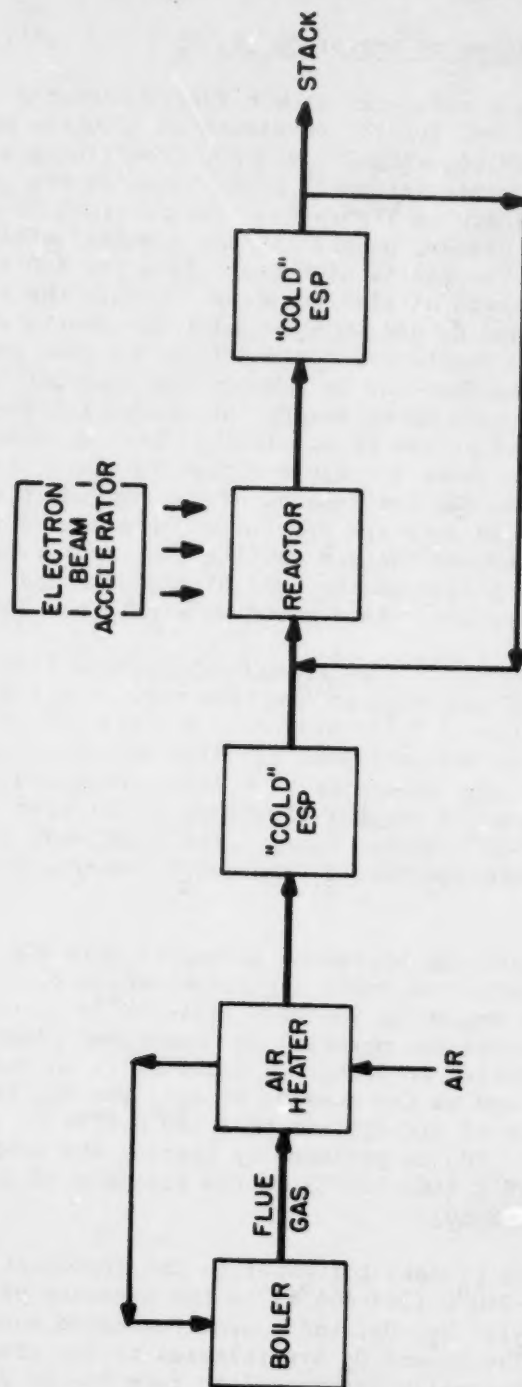


Figure 29. Flow Diagram of Ebara-JAERI Electron Beam Radiation Process.

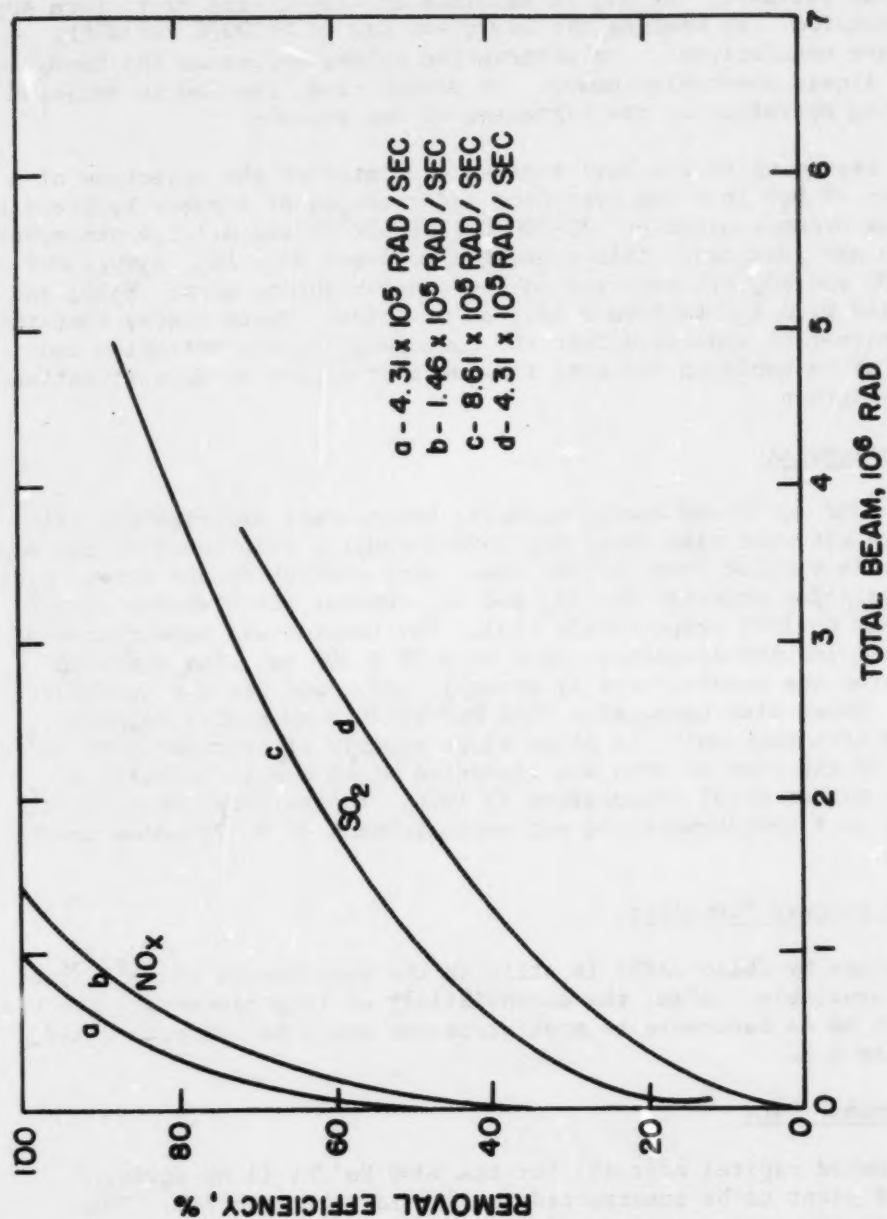


Figure 30. Effect of Beam Intensities on NO_x and SO₂ Removal Efficiencies for Ebara-JAERI Process (5).

A different byproduct treatment method combined the byproduct with CaO in the form of a paste. The paste is steam-roasted at a pressure of 0.1-1.0 atmosphere and temperature of 250-500°C (482-932°F) to create a gas stream of SO₂ and NO_x and a deposit of CaSO₄ and Ca(NO₃)₂. The gas stream of SO₂ and NO_x is recycled to the roasting section. By heating the residue of CaSO₄ and Ca(NO₃)₂ to 300-650°C (572-1202°F), NO_x and HNO₃ are formed leaving a CaSO₄ and CaO residue. The NO_x is oxidized at <140°C (284°F) to form NO₂ for HNO₃ production. By heating the CaSO₄ and CaO to >1300°C (2372°F), SO₂ and CaO are manufactured. An alternative scheme separates the CaSO₄ and CaO by heavy liquid separation means. In either case, the CaO is recycled to the blending operation at the beginning of the process.

Another system which was investigated consisted of the injection of a small quantity of H₂O into the byproduct and creation of a paste by blending. This paste was steam-roasted at 150-300°C (302-572°F) and 0.1-1.0 atmospheric pressure with air inserted. This operation produced SO₂, NO_x, H₂SO₄, and HNO₃. The SO₂ and NO_x are recycled to the steam-roasting step. H₂SO₄ and HNO₃ are cooled with H₂O to form a mixture of acids. Ebara states that this mixture may either be separated into the components by concentration and distillation or be employed for acid treatment of an ore or neutralization of alkaline solution.

Status of Development

In 10 Nm³/hr (0.003 MW equiv) capacity bench-scale experiments, oil-fired flue gas was used with inlet SO₂ levels ranging from 500-1500 ppm and inlet NO_x levels varying from 145-590 ppm. With various dosage rates, pressures, and radiation sources, the SO₂ and NO_x removal efficiencies ranged from 36-68% and 63-100% respectively (83). The reactor was constructed of stainless steel and the dimensions were 50 x 50 x 500 mm. The electron beam accelerator was manufactured by Hitachi, Ltd., and was the Cockcroft-Walton type. Ebara also operated a 1000 Nm³/hr (0.3 MW equiv) capacity, oil-fired gas treatment unit. A pilot plant capable of treating 3000 Nm³/hr (1 MW equiv) of gas from an iron ore sintering plant was to be built at Yawata Works, Nippon Steel Corporation in 1976. Future development should include tests on a prototype-scale and establishment of a byproduct treatment process.

Background of Process Developer

This process by Ebara-JAERI is still in the development stage and not commercially available. Also, the accessibility of this process to the U.S. market may not be as favorable as most processes since no contacts could be found in the U.S.

Published Economic Data

The estimated capital cost (5) for the 3000 Nm³/hr (1 MW equiv) capacity pilot plant to be constructed in 1976 is to exceed \$1M. This may not include any waste treatment facilities since none were tested in the 1000 Nm³/hr size unit. This cost exceeds \$1000/kW which is quite high but naturally will be reduced some with economy of scale. (Note: Proprietary

information received recently from other sources indicates the capital investment could be an order of magnitude less than reported by Ando (5). This lower capital investment may allow the process economics to be competitive with other simultaneous NO_x - SO_2 removal systems. The significant difference in order of magnitude has not been resolved.) No operating costs are given but the only major factor is the power consumption. However, it is stated by Ebara-JAERI that the most economical method of operating this process may be to remove the NO_x from the flue gas by this electron beam process (where lower intensity may be used) and then remove SO_2 by conventional FGD.

Raw Material, Energy, and Operation Requirements

No raw materials are necessary for this electron beam radiation since electricity is the only item claimed to be consumed. The power required for only an electron beam accelerator for a $100,000 \text{ Nm}^3/\text{hr}$ capacity unit (33 MW equiv) is estimated to be 1 MW. Therefore, the power usage for just the accelerators, thereby excluding the ESP consumption, is 3.3% of the equivalent total power output. The 1-MW size electron beam accelerator is possibly as large as will be available. If so, a 1-MW accelerator will be required for every $100,000 \text{ Nm}^3/\text{hr}$ of gas treated.

The manpower, technical support, and maintenance requirements are unavailable.

Technical Considerations

The process appears to be simple and direct but process control capability may be complex involving control of the accelerator based on inlet composition, temperature, and flow rate of flue gas. Figure 30 shows NO_x and SO_2 removal with a gas containing 80 ppm NO_x and 600-900 ppm SO_2 . The sensitivity of NO_x and SO_2 removal to inlet gas composition at two different pressures is shown in Figure 31. It is stated that the flue gas must contain at least 1% by vol of O_2 for efficient removal of NO_x and SO_2 , and it is preferable for the gas to contain a quantity of water vapor greater than or equal to that of NO_x . No estimate for comparative equipment size is available.

This process possibly could be applied to the retrofit of a plant with or without an FGD unit. If an FGD unit is present, this process may be used for only NO_x removal and a less intense beam may be used as shown in Figure 30 than for simultaneous removal. However, the capital cost may be prohibitive because the cost of the NO_x -only system would be essentially the same as for simultaneous NO_x and SO_2 removal case. If there is no FGD and only a cold ESP, the process would be used as described.

Since several acceleration and reactor units would be required for a 500-MW plant, for example, the major turndown capability would be the removal of units from service as needed. The recycle streams around the reactor would also provide some turndown control.

The only item known about materials of construction is that the bench-scale reactor used in the initial tests was made of stainless steel. The byproduct formed is corrosive to stainless steel when mixed with a small amount of water.

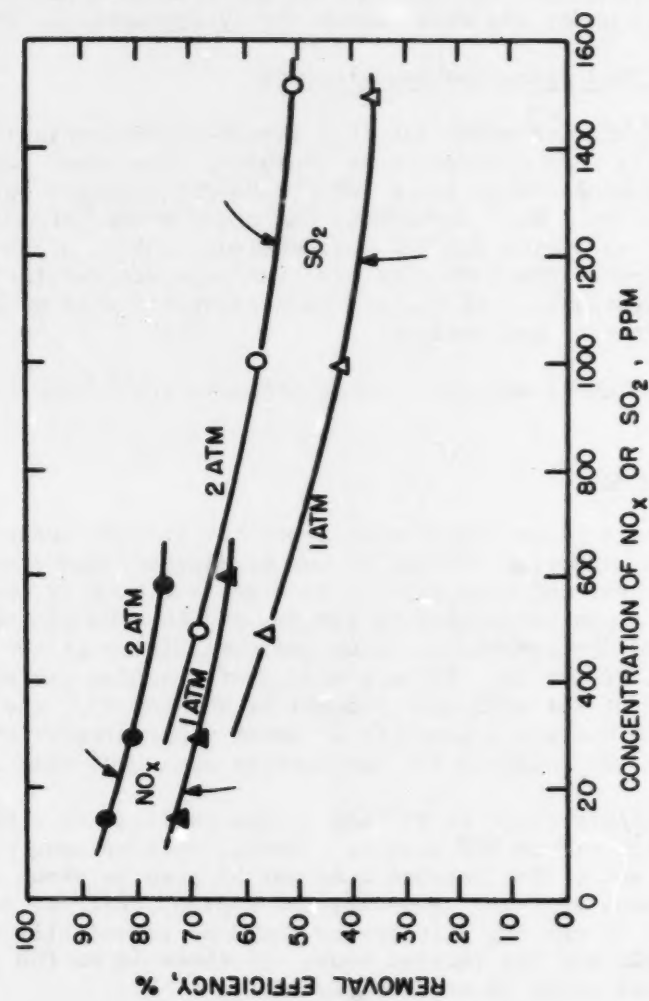


Figure 31. Relationships Between Inlet Gas Concentrations, Pressure, and NO_x and SO_x Removal Efficiencies for Ebara-JAERI Process (83).

Environmental Considerations

The electron beam radiation process removes SO₂ in addition to NO_x. As noted in Figure 30, the beam intensity required for SO₂ removal is higher than that for NO_x only. In general, higher rates of irradiation are less effective when used with gaseous materials. However, as shown in Figure 30, more effective NO_x and SO₂ removal are obtained with larger dosage rates in this process. Within a certain range of beam intensities, an applicable equation relating NO_x removal to total dosage rate is as follows:

$$a = 160b$$

where:

a = ppm NO_x removed by electron beam radiation

b = total dose in 10⁶ rad

Also, a higher pressure is more effective in removing the NO_x and SO₂ than a lower pressure as is pictured in Figure 31. Figure 32 displays the reactor residence time difference required for only NO_x removal compared to simultaneous NO_x and SO₂ removal. Though the NO_x can be almost completely removed within 2 sec, 10% of the SO₂ still remains after 10 sec of residence time.

Waste disposal will be required for the byproducts exiting the reactor and collected by the ESP. Whether any of the methods previously described are applicable for power plants will have to be proven in larger scale tests. The information obtained on the sensitivity of NO_x and SO₂ removal efficiency to various operating conditions is limited to that shown in Figures 30, 31, and 32. It is unknown if there will be any interference from gas species or the remaining particulates in coal-fired flue gas. The safety risks involved with this radiation process are also questionable.

Critical Data Gaps and Poorly Understood Phenomena

Included in the data gap is the maximum particulate loading allowable in the flue gas entering the reactor. It also needs to be known if there is any significant difference in removal efficiency for treating flue gas at 110°C (230°F) as reported herein and treating the gas at 150°C (302°F), the temperature which might be expected at the exit of the air heater on a coal-fired power plant. The chemical principles of this process are not given in detail.

The operating costs are not given but the consumption of electricity will essentially compose the entire operating expense of the NO_x and SO₂ removal section. The manpower, technical support, and maintenance requirements are not known, as is the materials of construction required except for the reactor vessel. Information is also lacking on the size of the reactor required for commercial-scale installations.

Handling of the byproducts formed will be necessary but the exact method is not determined. The potential for work hazards has not been ascertained.

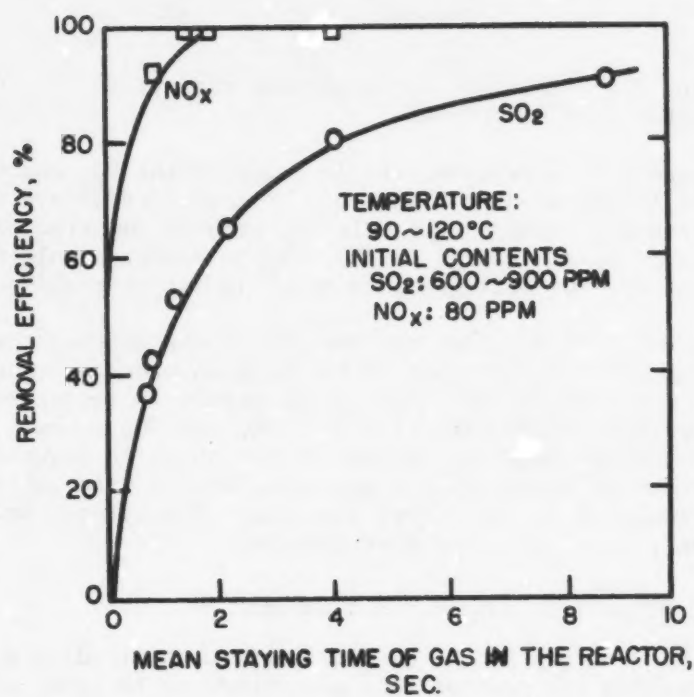


Figure 32. The Relation Between the Staying Time of Gas in the Reactor Chamber and the Removal of SO₂ or NO_x for Ebara-JAERI process (83).

Advantages and Disadvantages

The advantages and disadvantages are as follows:

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >90% NO_x removal efficiency
3. Operates between 100 and 200°C, which may require only negligible reheat
4. Does not require chemical raw materials

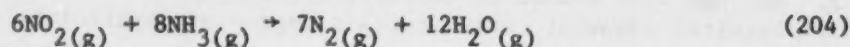
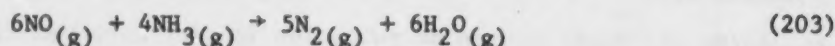
Disadvantages

1. Forms secondary source of pollution (powder composed of H, N, O, and S)
2. Has not been tested on coal-fired flue gas
3. Requires somewhat clean (certain degree of particulate removal needed) gas feed
4. Uses significant amounts of stainless steel or exotic materials for process equipment
5. May require very high capital investment (see note on page 165)

ENVIRONICS, INC. - ENERON CORPORATION - DRY, SCR OF NO_x

Process Description and Principles of Operation (67, 77, 78)

Environics, Inc., has been developing and has obtained a patent on an NO_x removal method which utilizes NH₃ to reduce NO_x to N₂ and H₂O in the presence of a catalyst. The work performed to date by Environics has been with gas- and oil-fired flue gas. The process flow for a coal-fired flue gas is shown in Figure 33. Since some problems were experienced with soot even with tests on oil-fired flue gas, the flue gas exiting a coal-fired boiler first passes through a "hot" ESP for particulate removal. NH₃ is mixed with the flue gas before entering the air heater-reactor vessel. The air heater contains the catalyst and in this vessel the NO_x is selectively converted to N₂ and H₂O by NH₃ according to the following reactions.



Following the reactor and air preheater the flue gas is sent to an FGD unit and/or the stack.

The optimum operating conditions and NO_x removal results based upon pilot-plant operations with oil- and gas-fired flue gas are as follows:

Gas-fired conditions

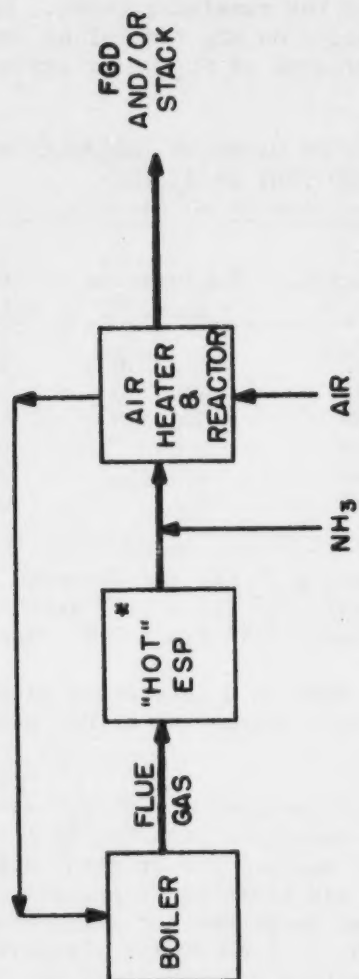
NO _x inlet concentration	125 ppm
NH ₃ inlet concentration	200 ppm
NH ₃ exit concentration	15 ppm
Reaction temperature	255°C (490°F)
Space velocity	50,000 hr ⁻¹
Catalyst	0.03% platinum by wt
NO _x removal efficiency	85%

Oil-fired conditions

NO _x inlet concentration	125 ppm
NH ₃ inlet concentration	300 ppm
NH ₃ exit concentration	Not measured
Reaction temperature	282-304°C (540-580°F)
Space velocity	35,000 hr ⁻¹
Catalyst	0.03% platinum by wt
NO _x removal efficiency	65%

Status of Development

Environics has performed tests for NO_x removal on gas-fired flue gas on a small scale with a furnace and on a laboratory pilot plant with a boiler and a utility pilot plant. Studies on oil-fired flue gas have been performed on the utility pilot plant and laboratory pilot-plant levels.



*ASSUMED NECESSARY BY AUTHOR FOR COAL-FIRED BOILER OPERATION

Figure 33. Flow Diagram of EnviroNics, Inc. - Enecon Corporation Process.

Initially, laboratory experiments were performed employing (1) a variety of catalysts and (2) bottled gas mixtures of NO in N₂ with flow rates from 100-300 sft³/hr. As shown in Table 24 an NO_x removal efficiency of 90-95% could be obtained employing copper oxide (CuO), platinum (Pt), or vanadium-based (V) catalyst. Since these tests indicated a greater activity with Pt, Environics concentrated on Pt catalyst during the remaining tests. Later a gas-fired furnace was used to study the effects on NO_x removal by temperature, space velocity, NH₃:NO_x mol ratio, and effects of SO₂ on activity of various catalysts.

TABLE 24. SUMMARY OF CATALYST PERFORMANCE:
NO (ABOUT 300 PPM) IN N₂ (67)

Catalyst	Space velocity, hr ⁻¹	Temperature range, °F	NO _x removal efficiency
CuO/Cr ₂ O ₃	10,500 ^a	600-700	95-98%
Ba/CuO/Cr ₂ O ₃	10,500 ^a	600-700	95-98%
Pt	17,500 ^b	600-700	15-52%
CuO/CoO	10,500 ^a	600	99%
V ₂ O ₅ /MoO	10,500 ^a	600-650	75-93%
Pt	40,000 ^c	500	90%

a. Catalyst bed dimensions = 1" dia x 2.0" deep (pellets).

b. Catalyst bed dimensions = 1" dia x 1.2" deep (pellets).

c. Catalyst bed dimensions = 3/4" dia x 2.0" deep (honeycomb).

A gas-fired boiler was next used in a laboratory pilot-plant study on catalyst life and effects of various parameters on NO_x removal. The catalyst-life test extended about 4200 hr.

Environics was awarded an EPA contract in January 1973 for demonstrating an NO_x removal process employing reduction with NH₃ in the presence of a Pt catalyst on a utility pilot-plant scale. The original scheme for treating flue gas from a gas-fired boiler was expanded to contain oil-fired testing. A 170-MW boiler of the Los Angeles Department of Water and Power was utilized for this study. A 150,000 sft³/hr (1.5 MW equiv) slipstream from this boiler was used for the pilot-plant operation and the platinum catalyst was incorporated in the air heater after removal of some of the heat transfer elements. Gas-fired operation extended over 2000 hr and an average NO_x removal of 85% was achieved. The oil-fired operation slightly exceeded 400 hr because of problems with maintaining a sufficiently high temperature, maintaining a constant gas flow, NH₄HSO₄ deposits, and soot deposits on the catalyst. The maximum flue gas rate attained was 110,000 sft³/hr and NO_x removal only averaged 50%.

As a result of the short-lived tests with the oil-fired boiler at the utility pilot plant, further work was accomplished on a 12,500 sft³/hr capacity laboratory pilot plant. Number 2 diesel fuel oil with 5% S was burned

with a space velocity of $50,000 \text{ hr}^{-1}$ and temperature range of $260\text{--}338^{\circ}\text{C}$ ($500\text{--}640^{\circ}\text{F}$) employed. The NO_x removal still averaged far less than during gas-fired operation.

Background of Process Developer

Environics actually began work in October 1972 on the contract for utility pilot-plant operation awarded by EPA. However, the literature search and small-scale studies on various catalysts was performed much earlier. In addition, in February 1975, a patent was granted to Environics for an NO_x removal method from combustion flue gases and in the presence of SO_2 . Eneron Corporation is a spinoff organization of Environics. Eneron is continuing work on NO_x removal. Environics is in receivership and not active at this time. This process has not been applied commercially. This system should be accessible to the U.S. market.

Published Economic Data

The estimated capital investment for NO_x removal facilities on a 480-MW size gas-fired boiler is reported by Environics to be about \$11/kW. The revenue requirements are stated as about 0.2 mill/kWh. These are 1975 costs with a U.S. location. The above figures (67) are based on the following Environics assumptions.

1. 480-MW plant with $50 \text{ Msft}^3/\text{hr}$ of flue gas
2. Inlet gas NO_x concentration of 125 ppm
3. Catalyst cost of \$1,000/ ft^3
4. NH_3 cost \$0.18/lb including tankage
5. Space velocity of $50,000 \text{ hr}^{-1}$
6. Catalyst installed in existing air heater
7. Catalyst bed replaced at 5-yr intervals with 25% of replacement cost of catalyst counteracted by precious metal reclamation
8. Cost of capital is 10%

It should be noted that in this case there is no ESP required since it is a gas-fired boiler and the catalyst is installed in the air heater so that a separate reactor is not included.

Raw Material, Energy, and Operation Requirements

Based on the same case and assumptions as mentioned above in the economic section, the amount of NH_3 required is approximately 5.5 short tons/day. No additional electricity or other energy requirements are needed for this gas-fired case since no ESP is used and the catalyst is located in the air heater; however, these energy requirements would be necessary for the assumed process on a coal-fired boiler shown in the flow diagram. It is estimated for the 480-MW gas-fired treatment case that less than one man full time is needed for maintenance.

Technical Considerations

The Environics NO_x removal method is similar to other simple dry processes. As concluded by Environics the process control could simply include the injection of NH_3 adjusted based on the amount of NO_x or NH_3 , or total of both, in the gas effluent.

The sensitivity of NO_x removal to inlet gas composition was demonstrated in the small-scale and pilot-plant tests. Plugging of the catalyst was experienced with soot from oil-fired flue gas in the utility pilot plant though Environics states that larger honeycomb support for catalyst, intermittent cleaning with air or water, and countercurrent operation of the air heater may reduce this plugging. However, this indicates the need for particulate removal prior to the catalyst for coal-fired operations which possess far greater particulate matter. Also, different results were obtained on the NO_x removal efficiency for the small-scale tests than on the operation of pilot plants in oil-fired tests. The small-scale test, using gas-fired flue gas which contained 300 ppm of injected bottled SO_2 , displayed an NO_x removal of 80% at 232°C (575°F) after 450 hr. For the oil-fired pilot plants, NO_x removal only averaged 50% and the maximum achieved was 65% at $288\text{--}316^\circ\text{C}$ ($550\text{--}600^\circ\text{F}$). The NO_x removal efficiency in one test decreased from 60 to 20% at 304°C (580°F) in only 60 hr. Environics concluded it was possible that the Pt catalyst was poisoned by some constituent of oil-fired flue gas, other than SO_2 . However, there is significant evidence from other sources (5, 72, 88) that SO_2 does reduce the activity of Pt catalysts.

The size of the reaction area required should be much less with the Pt catalyst than for most other dry processes. The space velocity of $35,000\text{--}50,000\text{ hr}^{-1}$ is much greater than any other process and the temperature of $282\text{--}304^\circ\text{C}$ ($540\text{--}580^\circ\text{F}$) is lower than most other systems.

If the placement of the catalyst within the air heater is practical for coal-fired operation, the process would be very suitable for retrofit application. This is doubtful though considering the particulate loading of coal-fired flue gas and problems of soot associated with oil-fired flue gas. This system may be applicable to retrofit after an FGD unit since little SO_2 would then be in the gas to be treated. However, reheat would be required.

With the catalyst placed within the air heater and designed for full load, the turndown capability may not be affected because as the load decreases, NO_x foundation decreases, though not necessarily in the same proportion. However, the turndown capability appears more limited than most other processes. Several problems and loss in removal efficiency occurred during pilot-plant operation with boiler load fluctuations resulting in lower than desirable reaction temperature.

There is apparently no special material of construction required with the catalyst located in the air heater. The preferred catalyst support is a ceramic honeycomb structure.

Environmental Considerations

The NO_x removal sensitivity to various operating conditions may be seen in Figures 34-41. Figures 34, 38, and 40 show data from small-scale tests with gas-fired flue gas. Data from laboratory pilot-plant operations are presented in Figures 35, 39, and 41 for gas-fired flue gas and in Figure 37 for oil-fired flue gas. Figure 36 reveals results from the utility pilot plant with gas-fired flue gas. NO_x removal sensitivity to the temperature, shown in Figure 34, indicates a peak NO_x removal in the 204-260°C (400-500°F) temperature range. Figure 35 demonstrates there is little difference in NO_x removal between 243°C (470°F) and 260°C (500°F) while the NH_3 in the exiting flue gas decreases rapidly as the temperature increases from 470-500°F. The maximum NO_x reduction occurs at 254-260°C (490-500°F) in Figure 36. With the oil-fired flue gas, Figure 37 exhibits that NO_x removal was optimum in the 282-304°C (540-580°F) range but it was significantly less at 321°C (610°F). The effects of space velocity on NO_x removal are indicated in Figures 38 and 39. Both reveal the expected decrease in NO_x removal as the space velocity increases. As the amount of NH_3 injected increases from 100-500 ppm in Figure 34, the NO_x removal is shown to increase at any one temperature. Figure 40 denotes the increase in NO_x removal and the constancy of the NH_3 concentration in the exiting gas at 500°F, as the NH_3 concentration in the inlet gas increases from 300-600 ppm. However, Figure 41 implies that if NH_3 concentration surpasses 250 ppm, the NH_3 in the effluent rises rather rapidly and there is no increase in NO_x removal. As mentioned previously Figure 35 suggests the amount of unreacted NH_3 is decreased as the temperature increases; and it also displays the increase in NO_x removal with the increase in NH_3 : NO_x mol ratio. NO_x removal increase with additional NH_3 in the inlet gas is also demonstrated in Figure 37.

There is no removal of pollutants other than NO_x . There is no significant amount of waste or byproduct produced as with wet processes. However, the formation of NH_4HSO_4 may present a problem which would require removal by cleaning with compressed air or water (as stated by Environics).

As noted earlier the NO_x removal results in testing with oil-fired flue gas were less than expected. Because of difference in results on small-scale tests with bottled SO_2 injection (80% NO_x removal) and laboratory pilot-plant experiments with oil-fired flue gas (50% average NO_x removal), Environics felt some gas species other than SO_2 was poisoning the Pt catalyst.

There are no apparent work hazards.

Critical Data Gaps and Poorly Understood Phenomena

The effects on air heater performance and subsequent boiler operation would appear questionable in placing the catalyst in the air heater. Also, if the catalyst were placed in a separate vessel ahead of the air heater for coal-fired operation, the high temperature (e.g., 375°C or 700°F) may result in lower NO_x removal efficiency (Figures 34 and 36).

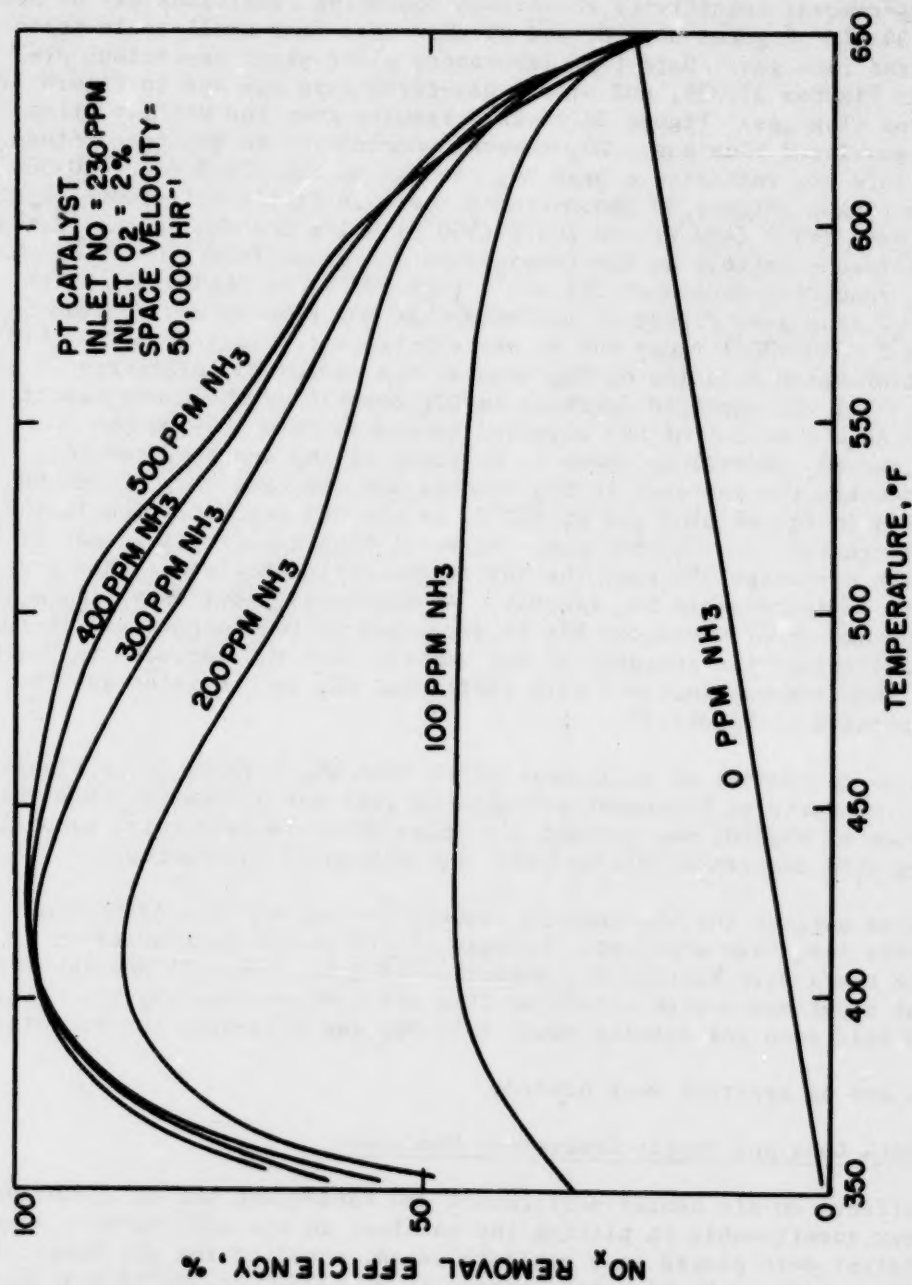


Figure 34. Effect of Temperature on NO_x Removal Efficiency for Eneron Process (67).

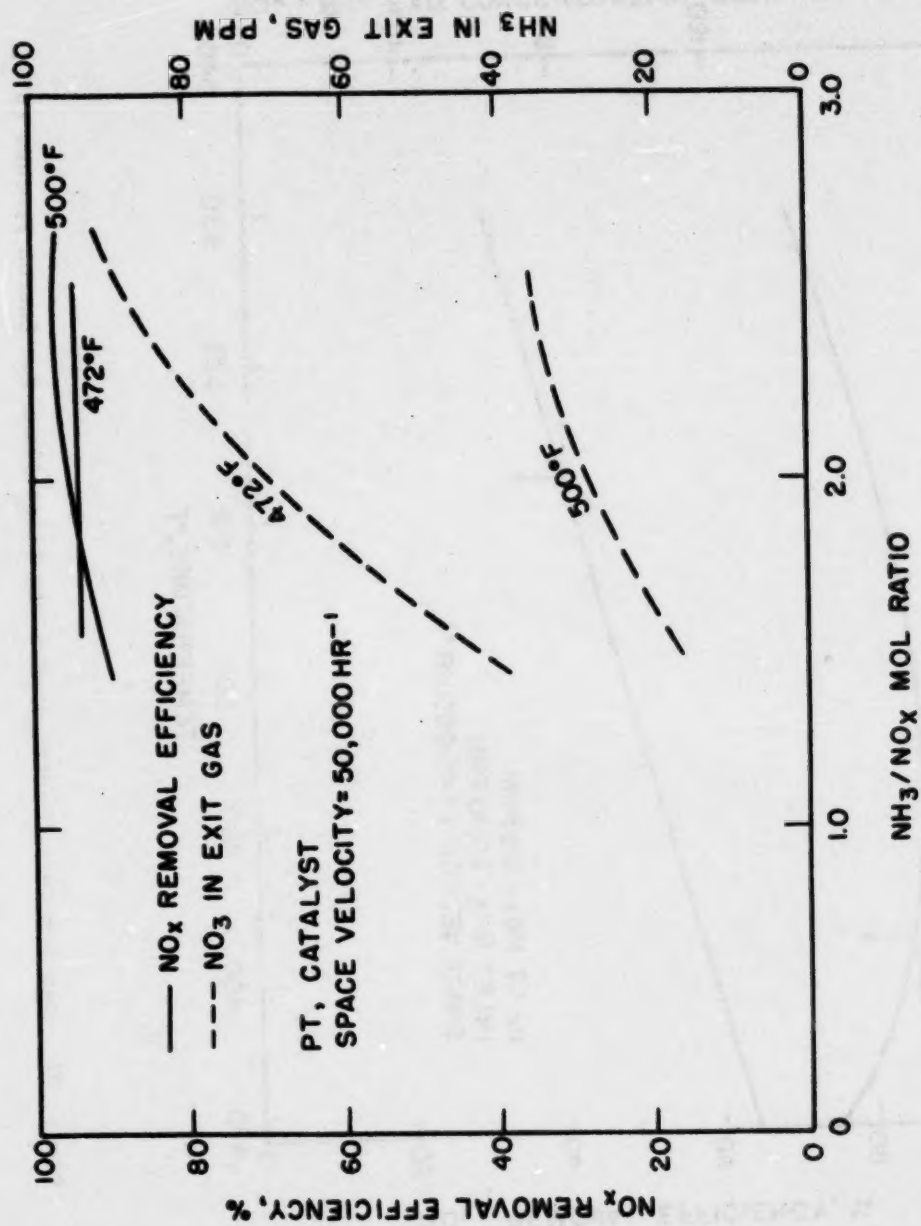


Figure 35. Effect of Temperature and NH_3/NO_x Ratio on Removal Efficiency for Enecon Process (67).

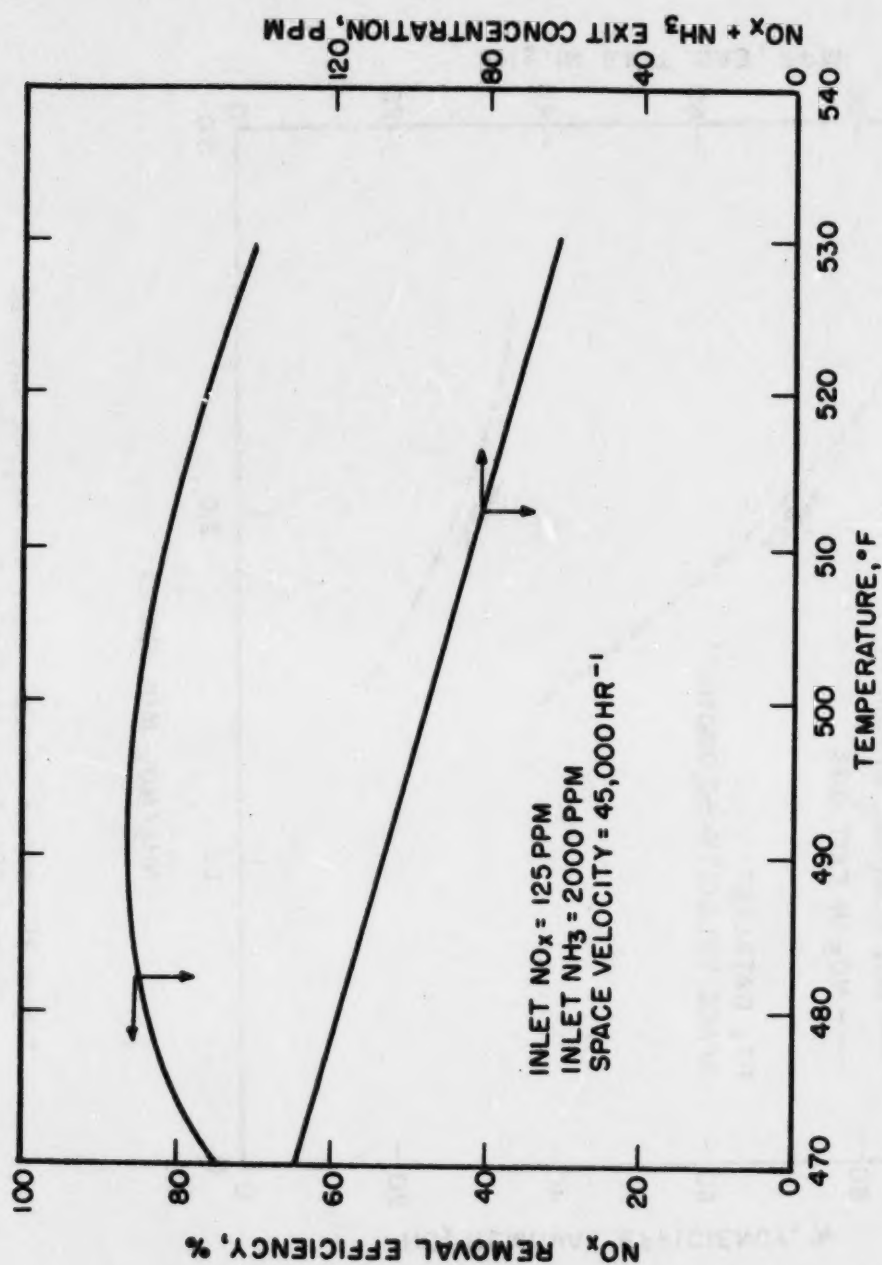


Figure 36. Optimum Test Conditions-Utility Pilot Plant for Enecon Process (67).

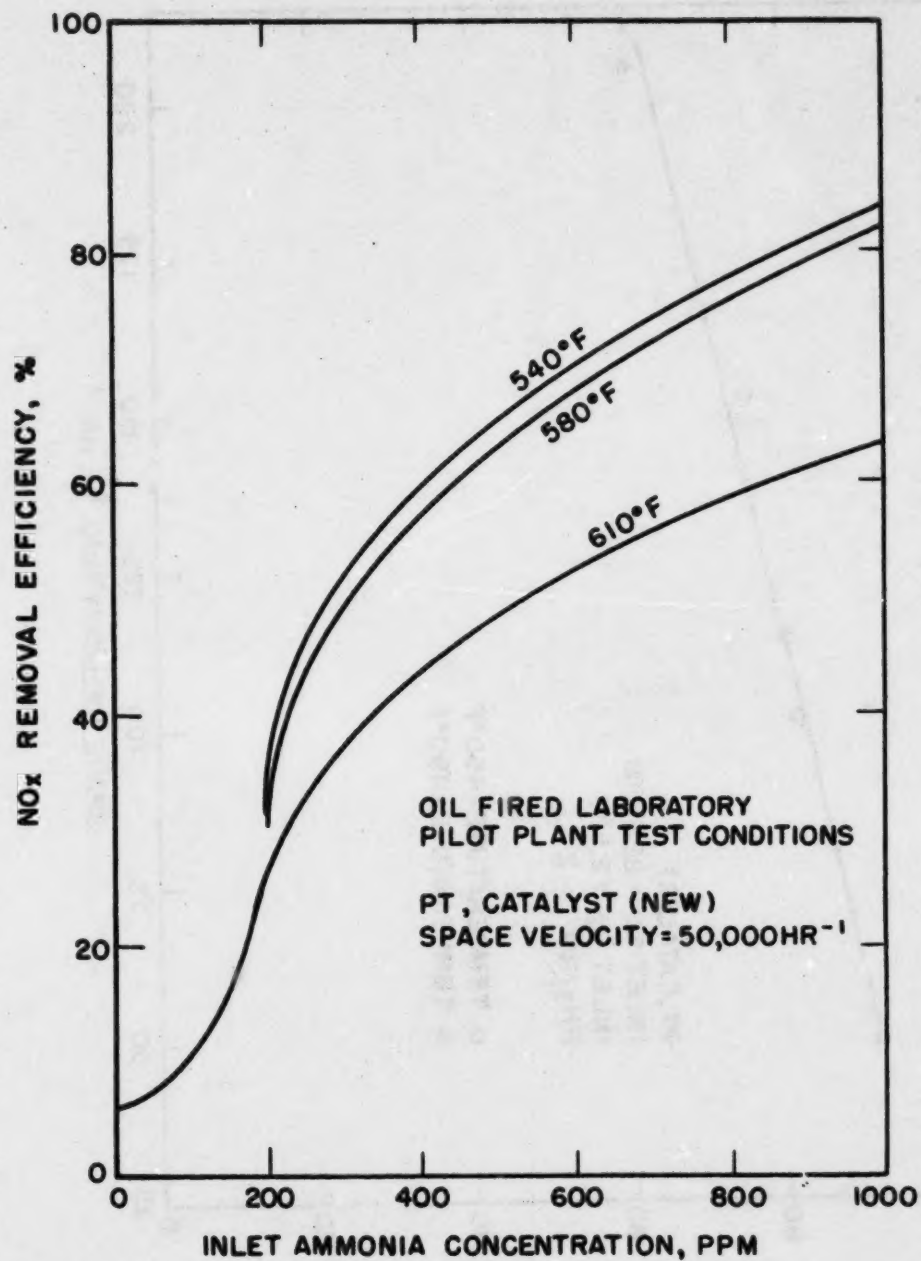


Figure 37. Effect of Inlet NH₃ Concentration on NO_x Removal Efficiency at Various Temperatures for Enecon Process (67).

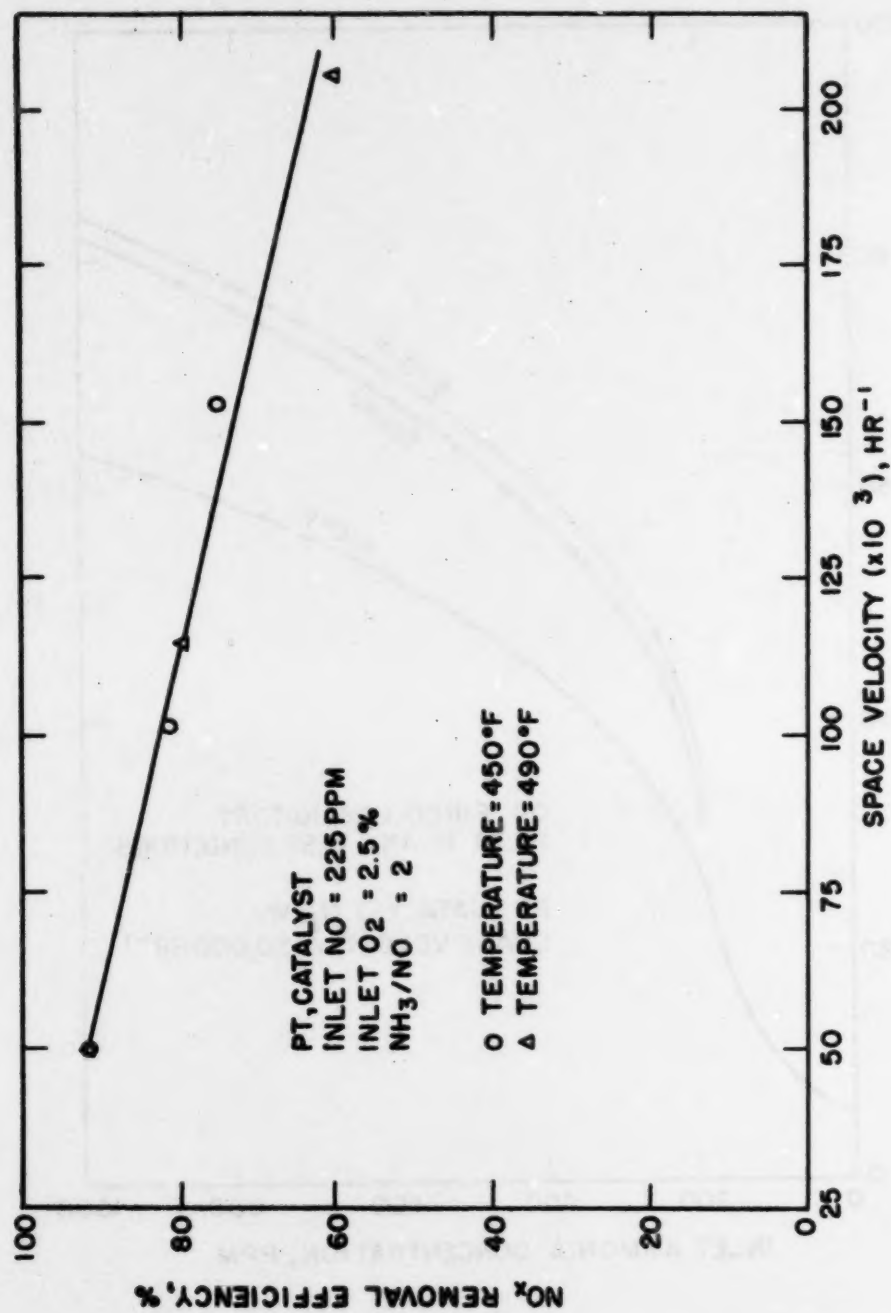


Figure 38. Effect of Space Velocity on NO_x Removal Efficiency for Enecon Process (67).

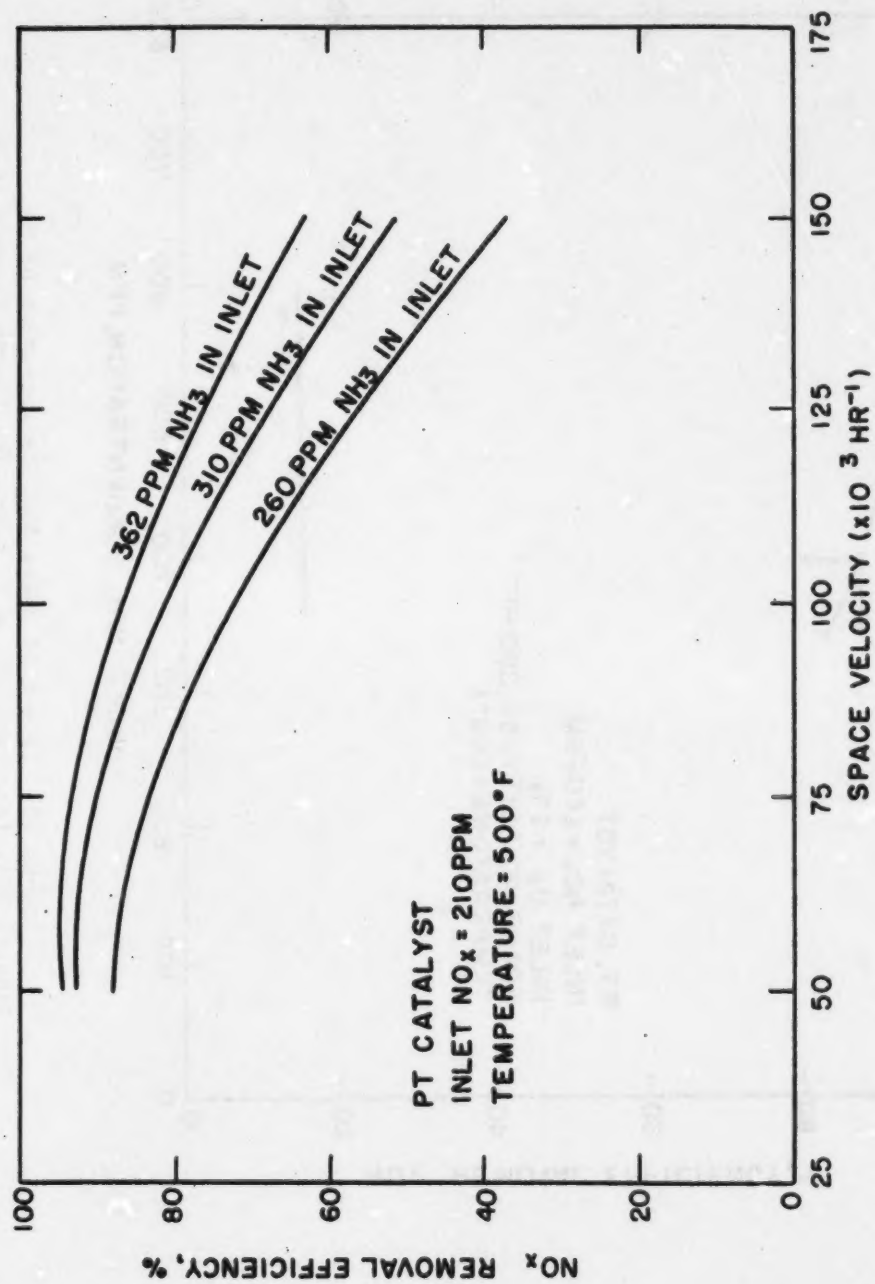


Figure 39. Effect of Space Velocity on Removal Efficiency for Enecon Process (67).

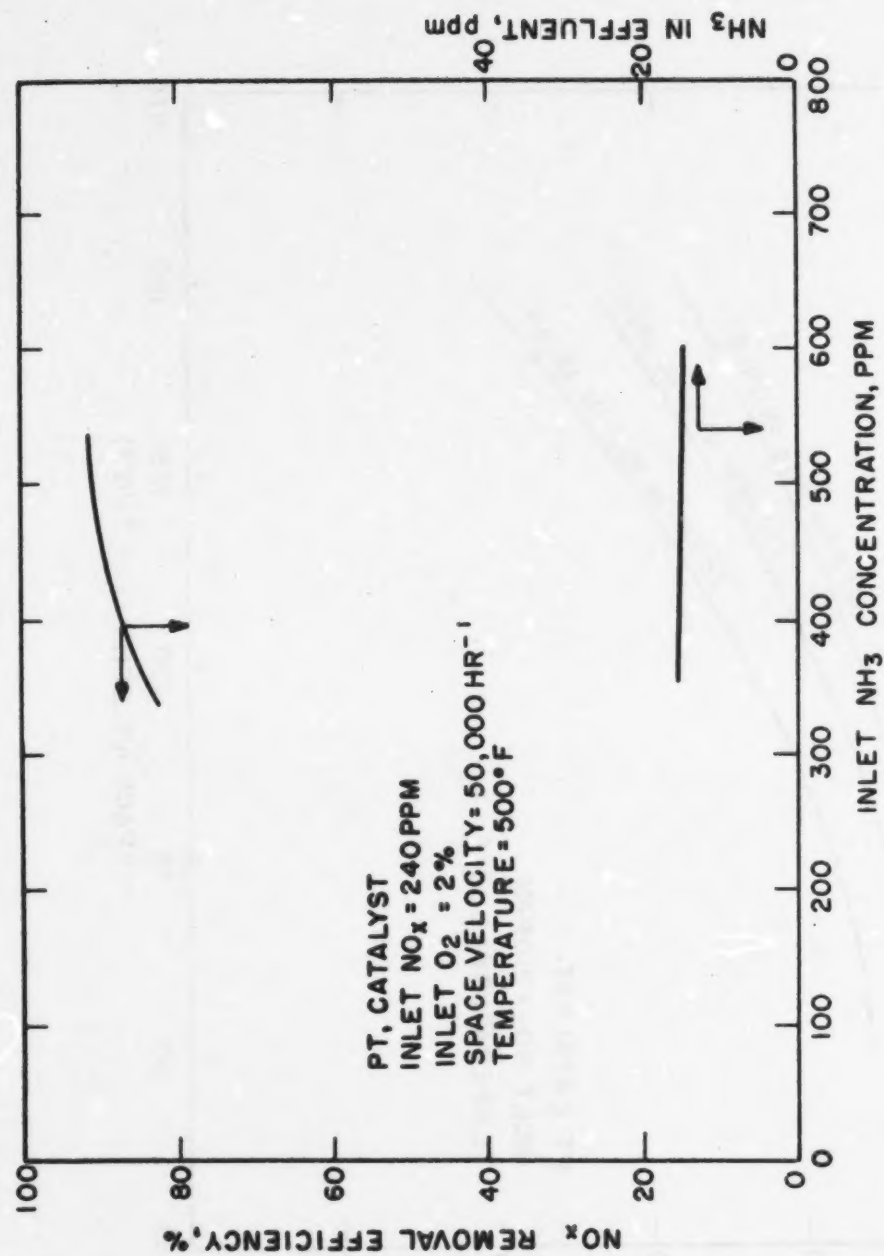


Figure 40. Effect of Inlet NH₃ Concentration on NO_x Removal Efficiency and NH₃ in Effluent for Enron Process (67).

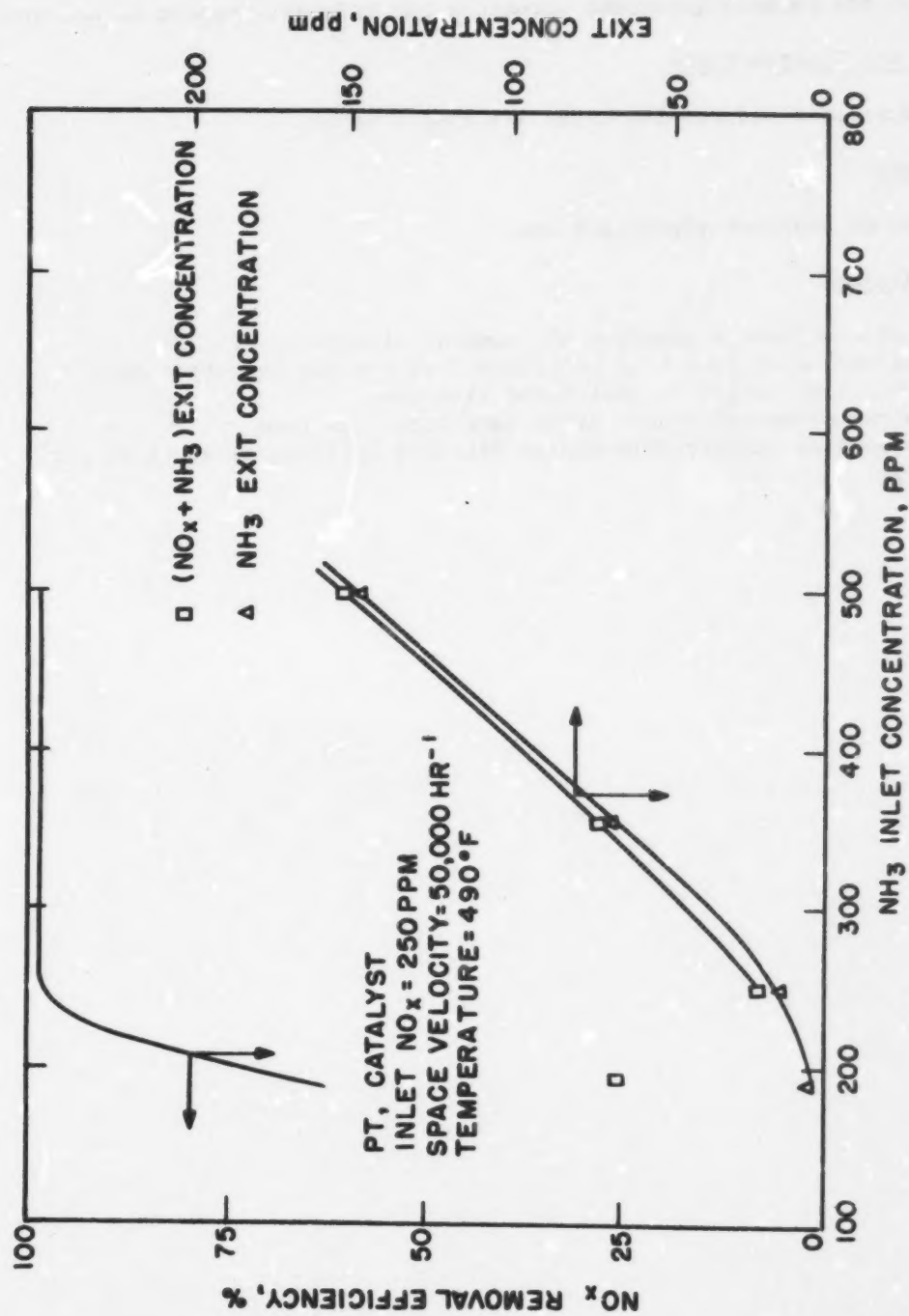


Figure 41. Effect of NH_3 on NO_x Removal Efficiency for Enecon Process (67).

Though the exiting gas NH_3 concentration is displayed from several tests on gas-fired operations, it is not shown for the oil-fired tests but is assumed to be quite high since the NO_x removal was much less than during tests with gas-fired flue gas. Also, the maximum particulate loading allowable for the process with the ceramic honeycomb structure for catalyst support is not stated.

Advantages and Disadvantages

The advantages and disadvantages are listed below.

Advantages

There are no apparent advantages now.

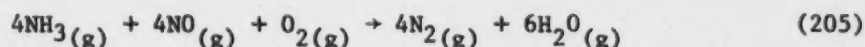
Disadvantages

1. Can only achieve a maximum NO_x removal efficiency of < 70%
2. Forms secondary source of pollution (>10 ppm NH_3 in outlet gas)
3. Has not been tested on coal-fired flue gas
4. Requires clean (SO_2 - and particulate-free) gas feed
5. Incorporates questionable design features (placing catalyst in air heater)

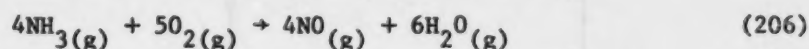
EXXON THERMAL DENOX PROCESS - DRY, SELECTIVE NONCATALYTIC REDUCTION (NO_x)

Process Description and Principles of Operation (6, 8, 79, 80, 81, 82)

Exxon has developed a thermal denitrification process (Thermal Denox) which selectively reduces NO_x by reaction with NH₃ without the use of a catalyst. NH₃ is injected directly into the boiler in the proximity of the steam superheaters and reheaters where the temperature is suitable for the reaction to occur. In a typical case, the temperature ranges from 1900°F (1028°C) prior to the secondary superheaters to 890°F (477°C) near the exit of the steam superheating section. A simplified flow diagram of this process is shown in Figure 42. This gas-phase homogeneous reaction involves a complex free-radical chain mechanism. However, the overall reaction may be written as follows:



The following competitive oxidation reaction also occurs.



A balance exists between reactions (205) and (206); though, in the applicable temperature range, a sizeable reduction of NO can be attained since reaction (205) is favored.

The optimum temperature range required with only the injection of NH₃ is 1700-1900°F (927-1028°C). By injecting a readily oxidizable gas, such as H₂ along with NH₃, the optimum temperature range for NO reduction can be lowered to about 1300-1400°F (704-760°C). An H₂:NH₃ ratio of <3 is preferred since excessive amounts of H₂ can decrease the selectivity for reduction of NO by NH₃. The H₂ may be injected either simultaneously with the NH₃ or at one or more intervals downstream from the point of insertion of NH₃. Figures 43 and 44 show data from laboratory studies for NO_x removal without and with the use of H₂ respectively.

A maximum of 70% NO_x removal has been obtained for commercial oil-fired boilers. An NH₃:NO_x mol ratio range of 3.0 to 4.0 was employed.

Status of Development

Initial laboratory experiments with this Exxon denitrification process used simulated mixtures of gases with helium (He) as a carrier gas. The gas mixture was sent through a quartz tube reactor located within an electric furnace. Operating conditions within the reactor included a positive pressure of 0.2 atmosphere, a temperature of 982°C (1800°F) and a 0.075 sec reaction time. The gas exiting the reactor was then analyzed. It was determined that above 0.5% O₂ concentration, the O₂ level had little effect upon NO_x removal. However, the NO_x removal became insignificant in the absence of O₂. The NO_x

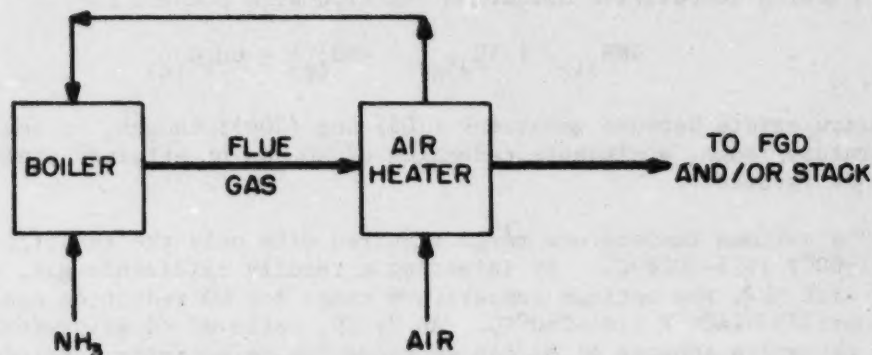


Figure 42. Flow Diagram of Exxon Thermal Denox Process.

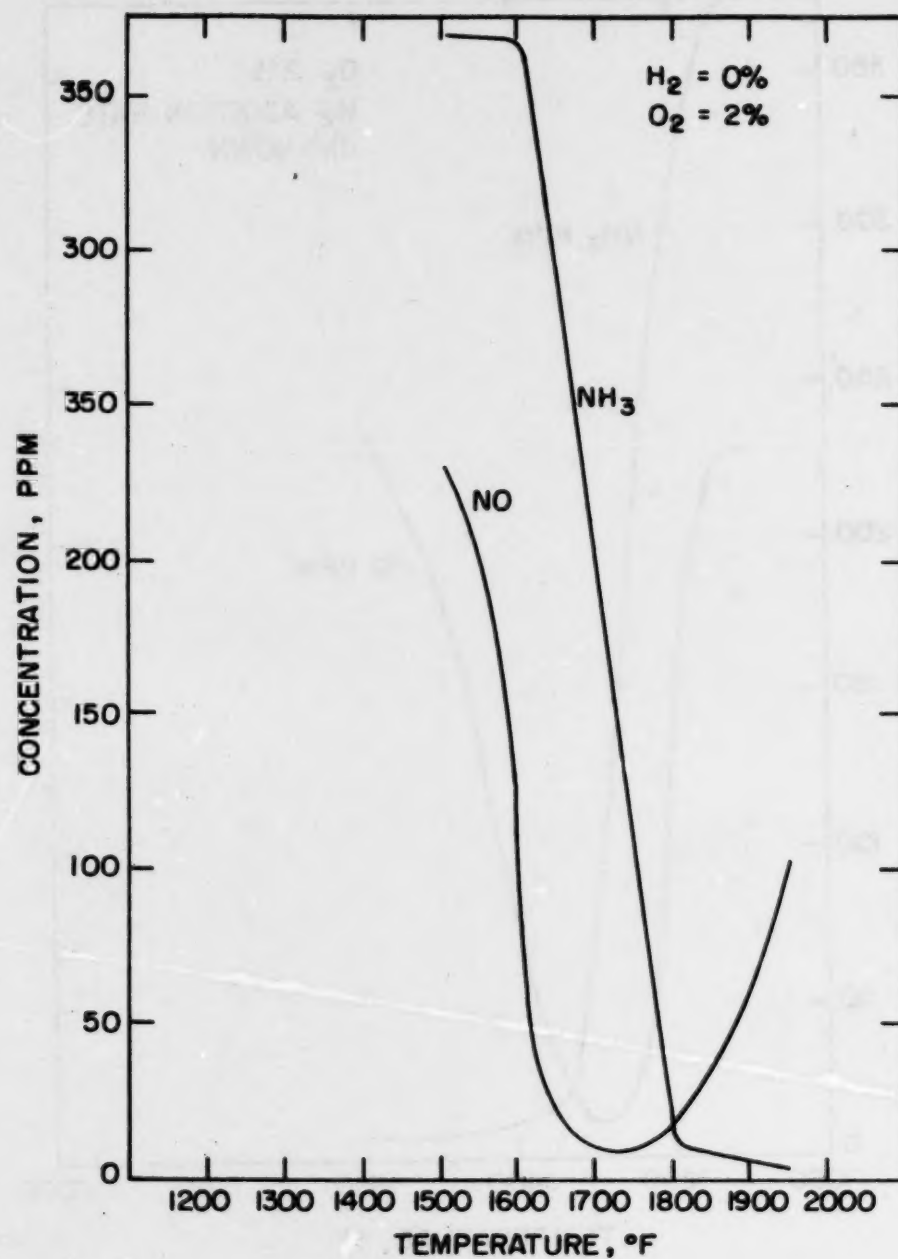


Figure 43. Effect of Temperature on NO Removal and NH₃ Concentration Without H₂ Addition for Exxon Thermal Denox Process (82).

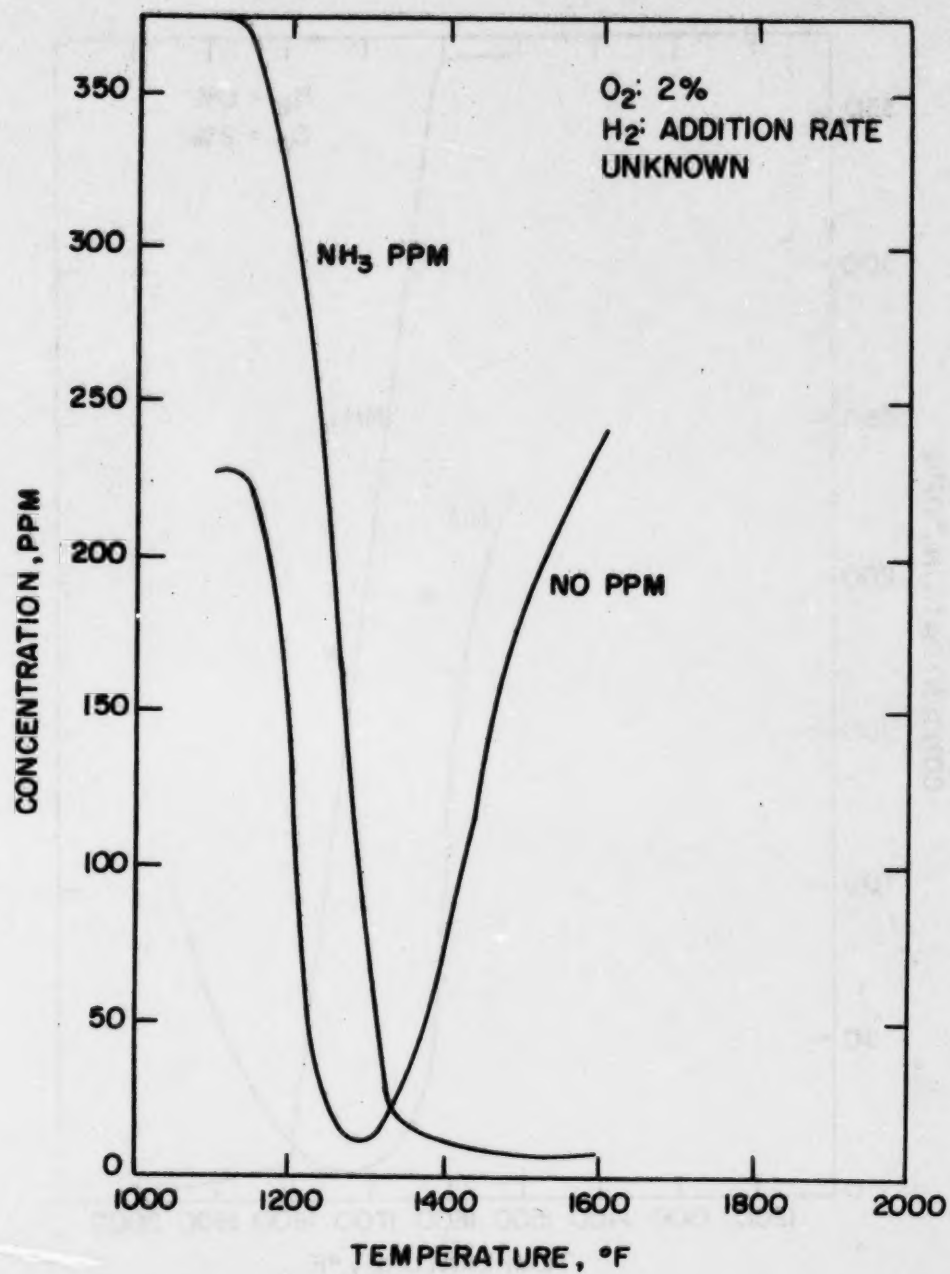


Figure 44. Effect of Temperature on NO_x Removal and NH_3 Concentrations with H_2 Addition for Exxon Thermal Denox Process (82).

removal at 0%, 0.5%, and 2.2% O_2 levels under laboratory operating conditions can be seen in Figure 45. It was also discovered that 1-2 mols of N_2O are formed by the reaction of NO with NH_3 and O_2 for every 100 mols of NO reduced.

This process has been demonstrated commercially at the Kawasaki refinery of Tonen Petrochemical KK, Exxon's Japanese affiliate. Tests were performed on an oil-fired boiler functioning up to a maximum of 140 MBtu/hr and a gas-fired furnace operating at 500 MBtu/hr. The boiler was operated as a swing boiler, replacing an out-of-service boiler, while the furnace functioned continuously. Up to 70% denitrification was obtained on these units with an NO_x concentration in the inlet gas of 150 ppm and an $NH_3:NO_x$ mol ratio in the range of 3:1 to 4:1 (see Figure 46). In addition to tests at the Kawasaki refinery, demonstrations have been performed in Japan on a municipal incinerator, 430 ton/hr oil-fired utility boiler, and a large pipestill furnace.

Background of Process Developer

This Thermal Denox process was developed by Exxon Research and Engineering Company, a subsidiary of Exxon Corporation. U.S. patent 3,900,554 covering this technology was granted to Exxon on August 19, 1975.

This process for NO_x removal is being licensed by Exxon to nonaffiliated companies. With the aid of Tonen Technology KK, Mitsui Petrochemical Industries, Ltd., acquired the first license in Japan. The technology was employed at its Chiba plant on a 120 ton/hr oil-fired boiler with >50% NO_x reduction attained.

This technology is readily available to the U.S. market.

Published Economic Data

The reported cost of Thermal Denox ranges from \$0.07 to \$0.15/MBtu fired on a retrofit basis and this includes the capital cost (82). This cost is based on a 60% NO_x reduction with an $NH_3:NO_x$ ratio of slightly greater than 2:1. Savings may be realized if the process is incorporated into the design of new equipment.

Raw Material, Energy, and Operation Requirements

The only raw materials needed for this process are NH_3 and H_2 . The use of H_2 for reducing the required temperature or for temperature compensation during a boiler fluctuation may not be practical for power plants from a safety aspect. It is estimated that 60 short tons/day of NH_3 is required to reduce 70% of the NO_x from the flue gas of a 500-MW plant containing 600 ppm NO_x with an $NH_3:NO_x$ ratio of 3:1 employed. The specific energy, operating manpower, maintenance, and technical support requirements have not been released by Exxon but should be minimal as compared to other NO_x removal processes.

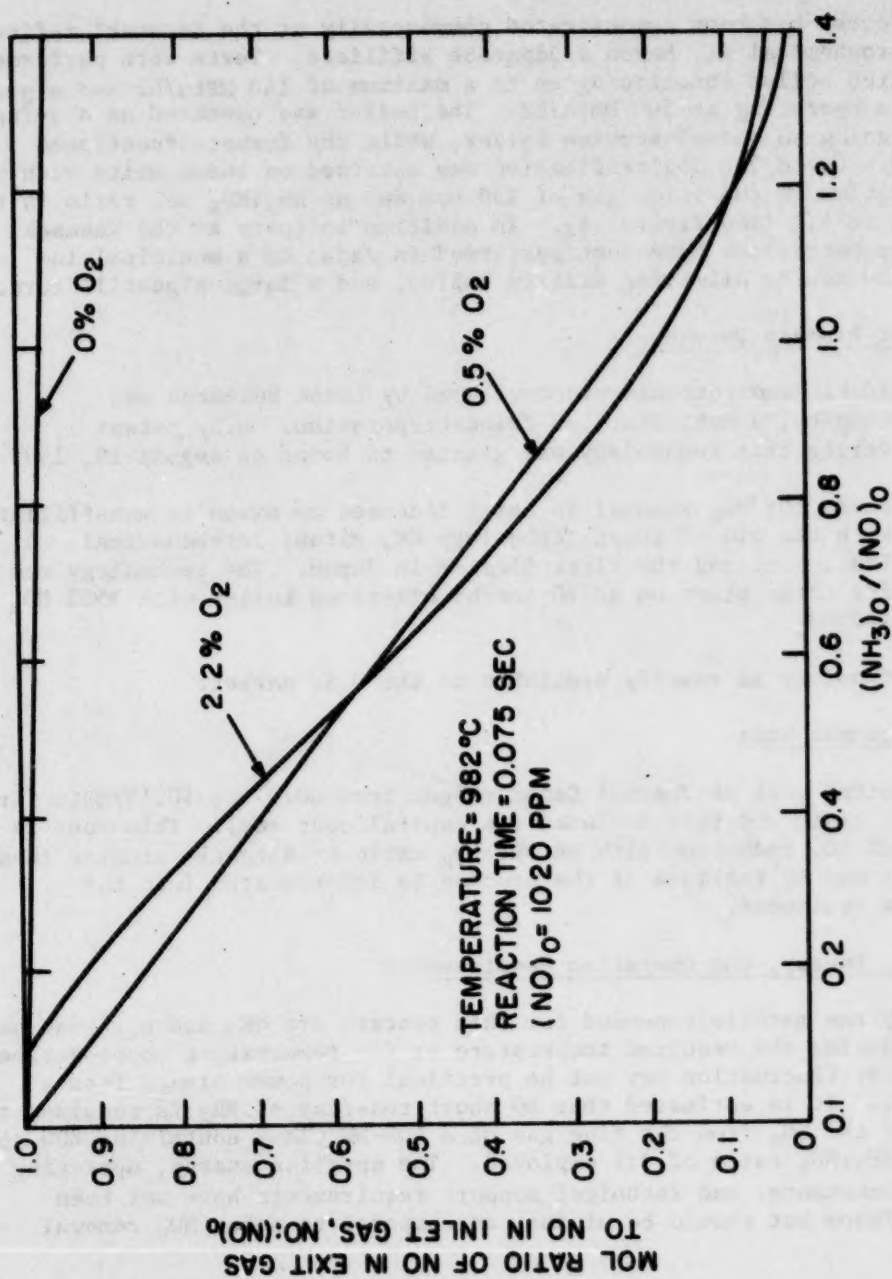


Figure 45. Effect of NH₃:NO Mol Ratio and Various O₂ Levels on NO Reduction for Exxon Thermal Denox Process (81).

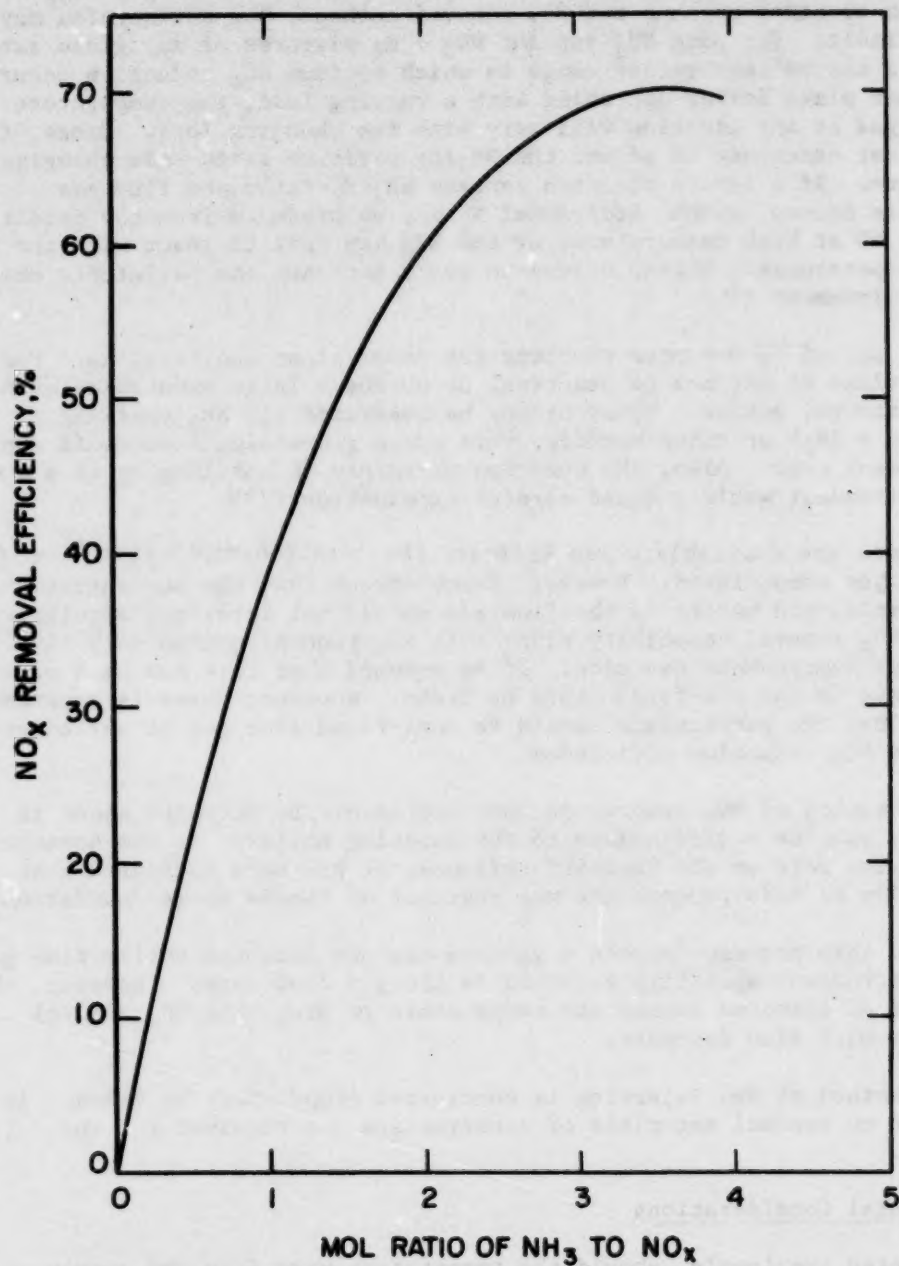


Figure 46. Effect of NH₃:NO_x Mol Ratio on NO_x Removal Efficiency During Commercial Tests for Exxon Thermal Denox Process (82).

Technical Considerations

Although the Exxon Thermal Denox process appears to be very simple in comparison to other dry and wet NO_x removal methods, its application may be very difficult. For pure NH_3 and for $\text{NH}_3 + \text{H}_2$ mixtures of any given ratio there is a narrow temperature range in which optimum NO_x reduction occurs. For a power plant boiler operating with a varying load, the temperature of the flue gas at any location will vary with the changing load. Hence, it would appear necessary to adjust the $\text{NH}_3:\text{H}_2$ ratio to match this changing temperature. If a severe mismatch between $\text{NH}_3:\text{H}_2$ ratio and flue gas temperature occurs, either additional NO may be produced from the oxidation of NH_3 to NO at high temperatures or the NH_3 may fail to react with the NO_x at low temperatures. Either occurrence would increase the pollutants emitted to the environment (79).

This use of H_2 may pose problems for power plant applications. For some locations it may not be practical to purchase large quantities of H_2 from an external vendor. While H_2 may be generated via NH_3 cracking ($2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$) or other methods, this added processing step would represent an additional cost. Also, the question of safety in handling H_2 in a power plant environment would require careful examination (79).

No data are available which indicate the relationship between NO_x removal and inlet gas composition. However, Exxon states that the concentration of SO_x or particulate matter in the flue gas should not interfere significantly with the NO_x removal capability since this NO_x removal method only involves a gas-phase homogeneous reaction. It is assumed that this has been proven with respect to the oil-fired tests by Exxon. However, there is apparently no proof that the particulate levels in coal-fired flue gas do not adversely affect the NO_x reduction efficiency.

This method of NO_x removal is most applicable to retrofit since it would only involve modifications to the existing boiler. At the commercial demonstration unit at the Kawasaki refinery, it has been indicated that installation of this process did not obstruct or impede normal operations.

Since this process injects a gaseous mixture into the boiler flue gas, the only turndown capability required is the gas flow rates. However, when the amount of turndown causes the temperature to drop, the NO_x removal efficiency will also decrease.

The method of NH_3 injection is considered proprietary by Exxon. It is known that no unusual materials of construction are required for the injection.

Environmental Considerations

As noted previously, should the temperature vary from the narrow temperature range required, an excessive amount of NH_3 and/or NO could be discharged out the system. In addition, it is possible for NH_4HSO_4 to be

formed from the combination of NH_3 , SO_3 , and H_2O in the cooler regions downstream of the reaction zone. This compound is capable of corroding as well as fouling equipment. Laboratory data indicated no difference in corrosion between presence of 45 ppm NH_3 and the absence of NH_3 . No additional corroding or fouling was noted during a lengthy run with NH_3 injection.

This process does suppress the oxidation of CO to CO_2 though it does not generate CO. So, if any CO is present when the NH_3 reduces the NO, it will remain and exit in the outlet gas. Exxon states that this is not a problem for oil- and gas-operated systems since the CO is completely oxidized to CO_2 before the gases arrive at the NH_3 injection point. However, it is unknown whether incomplete CO oxidation will pose a problem with coal-fired units.

Another species of NO_x which will exit with the treated gas is N_2O . For every 100 mols of NO reduced, 1-2 mols of N_2O are formed.

A potential work hazard is produced if H_2 is used to reduce the temperature required or control the NO_x removal during periods of variable temperature. The flammability limits are 4-7% H_2 for H_2 air mixture at atmospheric pressure (89). If small amounts of H_2 are used (e.g., $\text{H}_2:\text{NH}_3$ mol ratios <3:1) the risk may not be great. Also, Exxon indicates that the H_2 may be substantially diluted with inert gas such as spent steam. This dilution may further decrease the H_2 flammability hazard.

Critical Data Gaps and Poorly Understood Phenomena

Figure 44 shows the curve with an initial $\text{NH}_3:\text{NO}_x$ ratio of about 1.5:1. The results are not available for an $\text{NH}_3:\text{NO}_x$ ratio of about 3:1, which is a typical ratio for 60-70% NO_x removal in commercial application. Also, the $\text{H}_2:\text{NH}_3$ ratio used for this curve is not known.

Figures 43 and 44 indicate the relationships among NO_x removal, NH_3 emitted, and reaction temperatures at an initial $\text{NH}_3:\text{NO}_x$ ratio of about 1.5:1. It would be desirable to know the amount of NH_3 emitted at commercial conditions of 60-70% NO_x removal and ranges of $\text{NH}_3:\text{NO}_x$ ratios of 3:1 to 4:1.

The nature and technology of the NH_3 injection is proprietary information. The effects of particulates from coal-fired flue gas are uncertain though Exxon expects none.

The exact energy requirements are unknown. Also, the estimated labor, maintenance, and technical support requirements are unavailable.

Advantages and Disadvantages

The advantages and disadvantages of the Exxon Thermal Denox are as follows:

Advantages

1. Has been applied to flue gas from commercial oil-fired boilers
2. Operates with full particulate loadings ($>7 \text{ gr/sft}^3$)
(this is based on Exxon's expectation that particulate levels have no influence on NO_x removal efficiency but this has not been proven completely for coal-fired flue gas)
3. Requires no additional post-boiler processing equipment

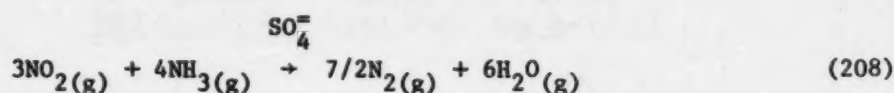
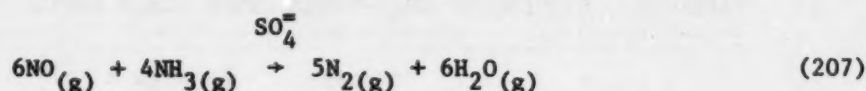
Disadvantages

1. Can only achieve a maximum NO_x removal efficiency of $<70\%$
2. Forms secondary source of pollution (large amounts of NH_3 or NO may be emitted)
3. Has not been tested on coal-fired flue gas
4. Incorporates design features which may present significant process control problems
5. Requires a relatively large $\text{NH}_3:\text{NO}_x$ mol ratio for equivalent NO_x removal ($\text{NH}_3:\text{NO}_x$ mol ratio of $>3:1$)

Process Description and Principles of Operation (53, 100, 114, 115)

Exxon has acquired two British patents for NO_x removal from gas streams. British patent 1,438,119 is concerned with the removal of NO_x and SO₂ from flue gas streams while patent 1,438,120 deals with removal of NO_x only from flue gas streams.

In the simultaneous NO_x and SO₂ removal process, a metal oxide catalyst combines with the SO₂ in the flue gas to form a sulfate. In the presence of this sulfate form of catalyst, NH₃ reduces the NO_x to N₂ as follows:



The harmless N₂ then exits with the flue gas. As the catalyst becomes converted to sulfates, the SO_x in the incoming gas is no longer removed and is found in the effluent gas. Regeneration of the catalyst is then required. In regeneration, a reducing gas mixed with steam is contacted with the catalyst to convert the sulfate to a free metal and to release SO₂. The free metal form of catalyst will be changed to the oxide form upon introduction of the flue gas. Some means of handling and utilizing the released SO₂ is required. The regeneration gas may range from 10-50% H₂ and 50-90% steam, but is preferably 40% H₂ and 60% steam.

The flue gas temperature required for this process ranges from 315-480°C (600-900°F). Temperatures of 315-370°C (600-700°F) may be expected for a coal-fired electric power generating facility. The most preferable NH₃:NO_x mol ratio utilized ranges from 0.7-1.0; Exxon states that increases in NH₃ usage above stoichiometric quantities do not result in significantly greater NO_x reduction. The space velocity would range from 2000-5000 hr⁻¹ and is limited by SO₂ removal rather than NO_x removal.

The NO_x-only removal method is very similar to the simultaneous NO_x-SO₂ removal system. The major difference is that continued regeneration of the catalyst in the sulfate form to release SO₂ is not required. The other operating parameters (i.e., temperature, space velocity, etc.) are similar.

Status of Development

The development information contained within the patents are limited to bench-scale experiments. For the simultaneous NO_x-SO₂ removal system, the first test involved the use of coal-fired flue gas containing 2500-3000 ppm SO₂, 400-600 ppm NO_x, 6.8% O₂ and small amounts of flyash. A total flue gas and NH₃ rate of 6.35 sft³/min with a space velocity of 2000 hr⁻¹ was

utilized. A 52-in.-long and 3-in.-diameter reactor with a fixed bed of CuO on Al₂O₃ was employed and an electrical heating jacket was used to cover the reactor. The catalyst was about 1.45% Cu by weight and the bed was 48 in. deep and occupied about 0.2 ft³. The operation of this system incorporated the following cycle:

1. 9-min NO_x-SO₂ removal period
2. 1/2 min, 1.25 sft³/min steam purge on reactor
3. 1-min regeneration period with 40% by vol H₂ and 60% steam at 0.4 g-mol/min of H₂
4. 1/2-min purge of the reactor with N₂ at a rate of 0.25 sft³/min

Some of the results obtained from these tests are shown in Table 25.

TABLE 25. RESULTS OF COAL-FIRED BENCH-SCALE TESTS (114)

ppm NO in inlet gas	Average NH ₃ :NO mol ratio	Average % removal over 9-min period ^a
542	1.0	78.4
542	1.47	84.2
553	3.2	92.4
553	3.5	86.8

a. Samples taken at 1-min intervals.

The SO₂ removal was maintained at 90-95%.

A second bench-scale experiment with the simultaneous NO_x-SO₂ removal process employed a synthetic flue gas comprised by volume of 2700 ppm SO₂, 1200 ppm NO, 5% O₂ and 0.6-2.0% H₂O. A 1-in.-diameter glass reactor containing a fixed bed of CuO supported on Al₂O₃ spheres with 8% by wt of Cu was used. The cycles utilized in this test were:

1. 30 min of NO_x-SO₂ removal
2. 1-min N₂ purge period
3. 2-min regeneration period with a gas mixture of 86% by vol H₂ and 14% by vol H₂O vapor
4. 1-min N₂ purge

The gas temperature and space velocity used were 343°C (650°F) and 5000 hr⁻¹ respectively. Both the relationship of NO removal to NH₃:NO mol ratio and the SO_x removal efficiency are demonstrated also by the results shown in Table 26.

TABLE 26. RESULTS OF BENCH-SCALE TESTS WITH SYNTHETIC FLUE GAS (114)

ppm NO in inlet gas	ppm SO ₂ in inlet gas	NH ₃ :NO mol ratio	% NO _x removal		% SO ₂ removal
			Entire 30 min	Last 23 min	
1,200	2,700	0.5	55.0	56.3	91.5
1,200	2,700	0.76	69.9	73.3	93.7
1,200	2,700	1.0	82.5	97.5	91.5

The NO removal is shown for both the entire 30-min NO_x and SO₂ removal cycle and for just the last 23 min. The entire 30-min NO removal average is always lower because during the first minute of the cycle, most of the catalyst is not in the sulfate form to aid the reduction of NO.

For the NO_x-only removal method, the bench-scale experiment was made using flue gas comprised by volume of 990-1010 ppm NO_x, 2700 ppm SO₂, and 3-5% O₂. The laboratory reactor was 7/8 in. in diameter and contained a 3-in.-deep catalyst bed of CuO supported on alumina. The space velocity employed was 5000 hr⁻¹. The relationship of NO_x removal to the gas temperature and NH₃:NO_x mol ratio is depicted by the results of the bench-scale investigation shown in Table 27.

TABLE 27. BENCH-SCALE RESULTS ON NO_x-ONLY REMOVAL (115)

NH ₃ :NO _x mol ratio	Gas inlet temperature, °F	% NO _x converted
0.25	650	35
0.33	650	45
0.33	750	50
0.38	650	52
0.4	750	55
0.5	750	75
0.67	650	95
0.67	650	95
0.73	650	100
0.8	650	100
0.8	750	100

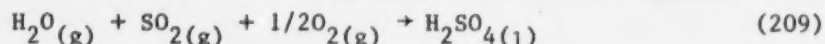
These NO_x reduction methods have been developed only in the laboratory and British patents have been obtained by Exxon on these processes. In personal communications with Exxon, it was discovered, however, that Exxon has no commercially available catalyst. Also, licensing of these processes are not being actively supported in the U.S. Thus, no greater detail is given to these Exxon processes.

FOSTLER WHEELER - BERGBAU-FORSCHUNG PROCESS - DRY, ADSORPTION (NO_x - SO_x)

Process Description and Principles of Operation (27, 28, 29, 30, 42)

The Foster Wheeler - Bergbau-Forschung (FW-BF) dry adsorption process removes NO_x as well as SO_x from boiler flue gas by adsorption on a special char. The adsorbed NO_x is reduced to harmless N_2 which is returned to the main flue gas and exits the stack. The SO_x is reduced to elemental S which is condensed as a byproduct.

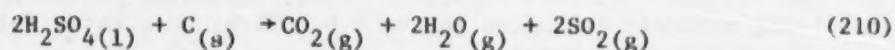
The FW-BF process consists of three sections: adsorption, regeneration, and off-gas treatment (RESOX). A flow diagram of the process is shown in Figure 47. Adsorption begins with flue gas, having passed from the boiler through the air heater and a highly efficient ESP, entering the adsorber. The adsorber is a vertical column with parallel louver beds containing a special activated char made from coal. The char is probably in pellet form with a diameter of 3/8 in. and a length between 3/8 and 5/8 in. Regenerated char is constantly being fed to a tank at the top of the adsorber and discharged through tubes to the individual char beds by gravity. In addition to carrying the moving char, the louvers direct the flue gas to flow cross-ways through the adsorption beds and out the adsorber to the stack. The SO_x and NO_x are adsorbed on the char which gradually but continuously progresses downward through the adsorber. As water vapor, O_2 , and SO_2 are adsorbed on the activated char, SO_2 is converted to H_2SO_4 by the following reaction.



This H_2SO_4 is then reported to be held within the char pellet pore structure. SO_3 is similarly adsorbed and, though NO_x is also adsorbed, the exact mechanism is still being studied both in the U.S. and in Germany. Particulate matter accumulates on the char pellet surface. The char flow rate is a function of the SO_x content of the flue gas but is slow enough to allow low char abrasion. Feeders at the bottom exit of the char bed regulate the char flow. The temperature in the adsorber is usually $121\text{--}149^\circ\text{C}$ ($250\text{--}300^\circ\text{F}$) and the optimum is $135\text{--}149^\circ\text{C}$ ($275\text{--}300^\circ\text{F}$). Therefore, if flue gas from a boiler exits the air heater at a temperature $>150^\circ\text{C}$ (300°F), tempering may be necessary to attain the optimum temperature. The pressure drop across the adsorber ranges from 4-10 in. of H_2O .

The saturated char exits the adsorber bottom onto the discharge feeders and proceeds to regeneration by a system of conveyors and bucket elevators. Screens, at the end of the conveyor and before the bucket elevators feeding char to the regenerator, sift the majority of the flyash deposit from the char pellets.

In the regenerator, the saturated char is blended with hot sand and the mixture slowly moves by gravity through the regeneration vessel. When the activated char reaches a temperature at or above 649°C (1200°F) the adsorbed H_2SO_4 reacts with the C to produce SO_2 as follows:



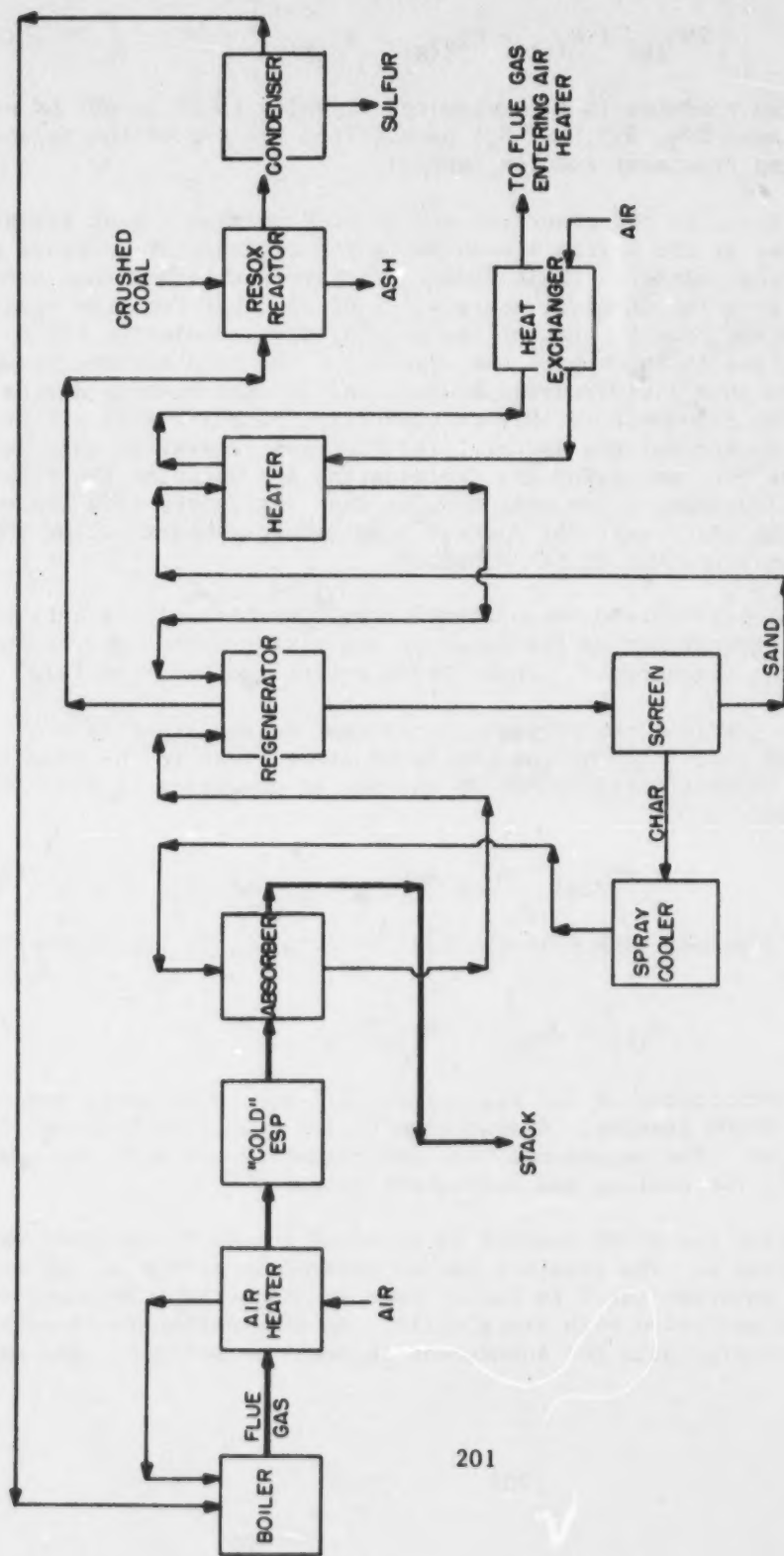
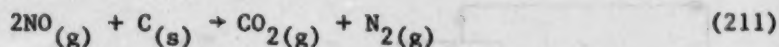


Figure 47. Flow Diagram of Foster Wheeler-Bergbau Forschung Dry Adsorption Process.

The adsorbed NO_x is converted to N_2 as follows:



The gas stream produced in the regenerator, which is 25 to 40% by wt SO_2 and the remainder CO_2 , H_2O , and N_2 , passes from the top of the regenerator to the off-gas treatment section (RESOX).

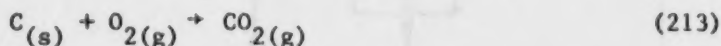
The sand is inert to the reactions and is used only as a heat transfer material. A feeder at the bottom discharge on the regenerator controls the flow of the sand-char mixture. This feeder discharges the sand-char onto a vibrating screen deck for physical segregation of the char from the sand. The char is collected from the top of the screen, spray cooled to 104°C (220°F), and recycled to the top of the adsorber. The sand passes through the screens, flows to a fluidized-bed heater, and is subsequently discharged and returned to the regenerator. Direct combustion of No. 2 fuel oil or coal is the heat source for the heater. The flue gas created in this heater is used to preheat the combustion and fluidization air entering the fluidized-bed heater. The flue gas, containing SO_2 , is then introduced into the main flue gas before the air heater for further heat recovery and to allow the SO_2 produced to be recovered in the adsorber.

The remaining particulate not screened from the char pellets between the adsorber and regenerator is dislodged by the mixing action of the char and sand within the regenerator. This flyash enters the hot sand loop.

The SO_2 -rich gas from the regenerator is sent to the RESOX reactor containing crushed coal. As the gas passes countercurrent to the flow of crushed coal, at $649\text{--}816^\circ\text{C}$ ($1200\text{--}1500^\circ\text{F}$) the SO_2 is converted to elemental S and O_2 as follows:



The resulting O_2 combines with C in the coal to form CO_2 by the following reaction:



The other constituents of the regenerator off-gas, such as N_2 and CO_2 , are inert in the RESOX reactor. A discharge feeder regulates the coal flow through the reactor. The unconsumed coal and resulting ash exit the reactor and enter a vessel for cooling and subsequent disposal.

The gas exiting the RESOX reactor is directed to the S condenser where S vapor forms molten S. The liquid S can be handled in either of two ways. One method is to maintain the S in liquid form for tank-truck shipment in an insulated tank outfitted with steam coils. An alternative is to solidify the liquid S in cooling pits for subsequent shipment as solid S. The gas

exiting the condenser contains CO₂, H₂O, N₂, and S not in elemental form. This gas is returned to the boiler, where the nonelemental S is oxidized to SO₂, and becomes a portion of the flue gas entering the adsorber.

The average NO_x removal efficiency with this FW-BF dry adsorption process is 40-60% and the SO_x removal efficiency averages 80-95%. The additional particulate removal efficiency on a gas having >99% of particulates removed by ESP is 90-95%.

The present information on conditions and flow rates is limited to data from brief tests at a prototype plant at the Scholz Steam Plant of the Gulf Power Company at Sneads, Florida, which had a 20-MW-equiv adsorber section and 40-MW-equiv regeneration and RESOX sections (see Status of Development). This information is as follows:

Item	Average or range
Gasflow to adsorber	174,000 lb/hr
Charflow rate through adsorber	5,300 lb/hr
Gas residence time in adsorber	13 sec
Char dwell time in adsorber	96 hr
Charflow rate to regenerator	5,300 lb/hr
Sandflow rate to regenerator	180,000 lb/hr
Sand to char ratio (vol)	13.9:1
Coalflow to RESOX reactor	100-250 lb/hr
Gasflow to RESOX reactor	750-2,000 lb/hr

Status of Development

BF has been involved in developing a dry adsorption process for desulfurization of flue gas since 1965. An activated char manufactured easily and inexpensively from bituminous coal was made which possessed the following attributes: (1) excellent SO₂ adsorption capability, (2) good physical strength, (3) low pressure drop, and (4) high ignition point. Experience on bench-scale tests and semipilot-plant tests led to extensive work on a 105,000 sft³/hr capacity pilot plant at Welheim, Germany. The flue gas for the pilot plant was a slipstream from a coal-fired steam generator. This plant was operated over 2 yr and with one continuous period of 6000 hr. It was discovered that this system also removed NO_x and particulate matter as well as SO_x. NO_x removal efficiency from small-scale pilot plants in Germany averaged 40-60%.

FW received full licensing rights to supply this process under BF skill and patents. Tests on small pilot plants in Livingston, New Jersey, and in Japan also averaged 40-60% NO_x removal. The construction of a 20-MW prototype unit of this adsorption process for treating coal-fired flue gas was completed in May 1975 at the Scholz plant as part of a technology evaluation program for Southern Company (holding company for several electric utilities). At present, testing has been short-lived because of equipment problems. The NO_x removal averaged only 25-30% but problems were experienced with NO_x monitoring equipment. The removal of SO_x averaged >96%.

Background of Process Developer

BF is the research institute for the German bituminous coal industry. As noted earlier, BF has been performing research on this adsorption process for many years. In addition to the pilot plants noted previously, BF is operating a 150,000 Nm³/hr capacity (50 MW equiv) desulfurization demonstration unit at Kellermann Power Station owned by Steinkohlen-Elektrizitat AG (STEAG) in Lunen, Federal Republic of Germany. The flue gas source is a slipstream from a 350-MW coal-fired boiler.

FW manufactures steam generating equipment and is a contractor to process plants. FW became very familiar with the BF adsorption process during technical and economic assessments of pollution control systems by the FW research department. Eventually, FW obtained licensing rights on the BF dry adsorption system.

This simultaneous NO_x:SO_x removal process is still in the development stages though it has been operated on coal-fired flue gas at several pilot plants. Arrangements are being made to continue the study at the Kellermann plant by the addition of a RESOX unit to the existing prototype BF plant.

Since FW is a licensing agent this process should be readily available to the U.S. market.

Published Economic Data

The estimated capital costs for an FW-BF adsorption system treating flue gases from plants of >200-MW equiv are reported to range from \$40/kW for 0.9% S-containing fuel to \$90/kW for fuel with 4.3% S (27, 28). Corresponding operating costs fluctuate from 1.0-2.3 mills/kWh with the same respective fuel-S contents (27, 28). These values are 1977 costs for a U.S. location. FW states that a graph of capital costs (\$/kW) vs MW rating and % S in fuel indicates the most economical utilization of this process in the 150-200-MW range. Beyond 200 MW there is little change in the economics. In cases of <50 MW, it is emphasized that several small boilers could be connected to an individual treatment system and the economic situation be improved by the overall rating of the system.

Raw Material, Energy, and Operation Requirements

The main raw material and utility requirements are water, makeup char and sand, crushed coal, auxiliary fuel, and electricity. The consumption and usage of the above are not yet available.

Maintenance requirements on this system are expected to be greater than for other dry systems which use fixed beds or, at least, equipment with fewer moving parts. Several mechanical problems caused trouble at the Scholz pilot plant with adsorber-bed levels, char-sand separation, hot sand conveying, char cooling, and char feed. However, several modifications were made to correct the above problems. Labor and technical support requirements are not known.

Technical Consideration

The FW-BF dry adsorption process is more complex than most other dry processes as indicated by the large number of processing steps and generally the flow of solids is more difficult to control as compared to the flow of gases. The flow rate of the solids is controlled by the discharge feeders on vessels, such as the adsorber, regenerator, and RESOX reactor. The flow of char into the adsorber beds from the surge tank on top of the adsorber is monitored with a level detector.

Little information has been obtained on the NO_x and SO_x removal sensitivity to inlet gas composition. At the Scholz plant prototype unit an average SO_x removal of 96% was maintained as the inlet flue gas SO_x composition varied from 900-2150 ppm. Figure 48 shows laboratory data on NO_x removal at a 720 ppm NO_x level in the inlet gas.

At the Gulf Power unit, the adsorber has two char-bed stages. Eight parallel vertical beds (6 ft x 6 ft) form the first stage and four similar beds (4 ft x 4 ft) are contained in the second stage. All beds are about 40 ft tall. The regeneration vessel used in this process has been in commercial application, i.e., at a coke production facility by BF for over 5 yr; therefore, most of the design and operational difficulties have been overcome. Also, the fluidized-bed heater has been used by many process industries for several years.

This system would obviously not be suitable for retrofit on a plant with an existing FGD since this process mainly removes SO_x from flue gas and NO_x removal is only secondary.

Turndown capability could be maintained to a limit by reducing flow rates of char, sand, and crushed coal through the respective vessels. However, a point could be reached where low gas and solid rates would interfere especially with regeneration and RESOX operation. Several trains would probably be required for a 500-MW size plant and trains could be removed from service as needed for the necessary turndown capability.

Materials of construction are carbon steel for the most part with some stainless steel being utilized in certain high-temperature areas.

Environmental Considerations

The only information obtained on removal efficiency sensitivity to operating conditions is indicated in Figure 48 which shows NO_x removal vs space velocity on a bench-scale apparatus.

The FW-BF adsorption system removes SO_x as well as NO_x and some particulates. An average of 96% SO_x removal has been obtained in pilot-plant runs and an average of 40-60% NO_x removal is expected. The maximum particulate removal is to be tested at the Kellermann plant unit by varying the ESP efficiency which controls the particulate load of the gas entering the adsorption system.

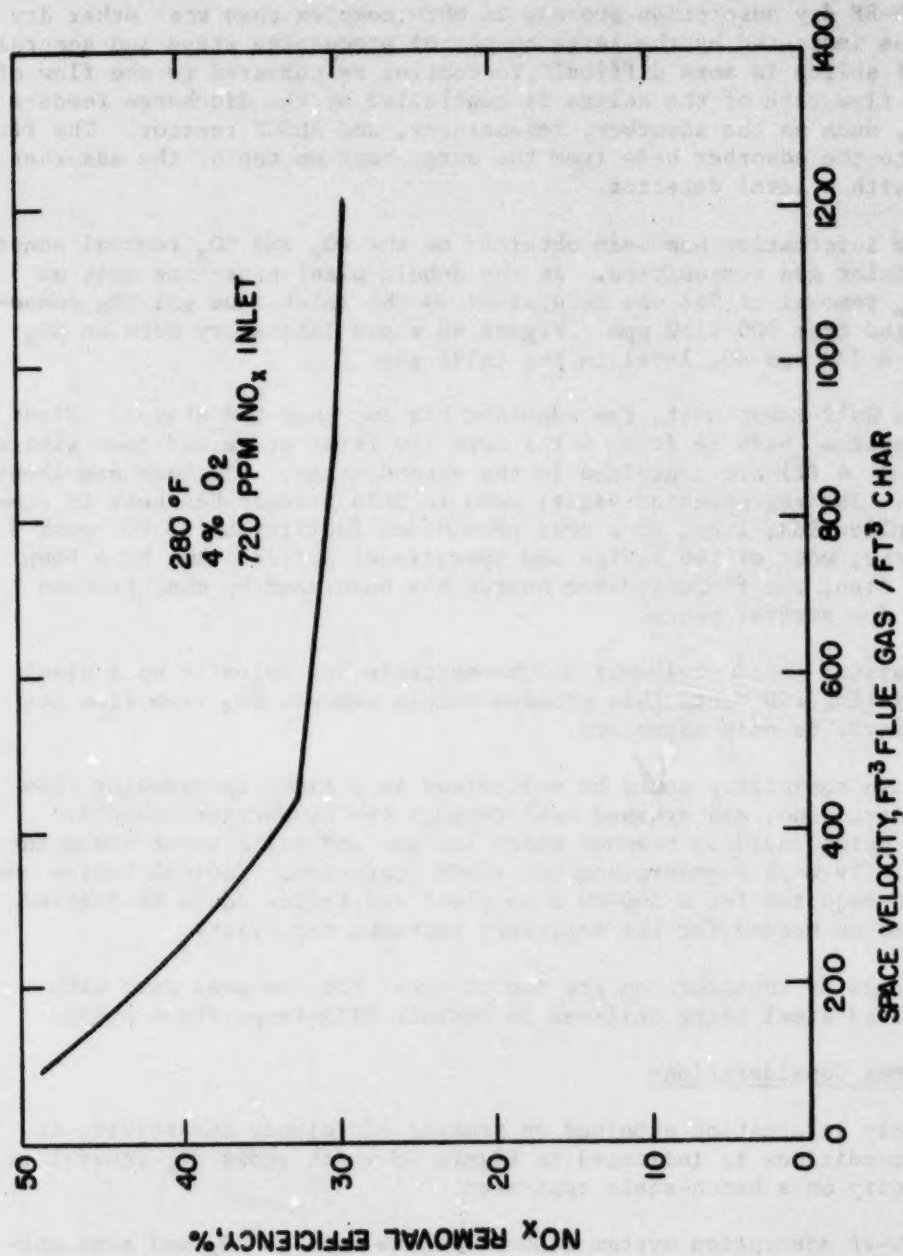


Figure 48. Effect of Space Velocity on NO_x Removal Efficiency for FM-BF Process (42).

All the streams in this process except the main flue gas, S byproduct, and crushed coal entering RESOX reactor are closed loop. So, there is no waste disposal needed other than for the ash created in the process.

There is no information on the interference of any gas species and contaminants.

In pilot-plant tests poor distribution of char to adsorber beds led to problems of char stagnation, resulting in local hot spots within the adsorber which not only reduce efficiency but could create a dangerous work hazard. However, the new char distribution and surge tank above the adsorber with feed lines to each bed is said to have corrected this problem. Additional temperature monitoring of both gas and char throughout the adsorber is provided now. Handling of molten S could be a minor hazard not found in the other processes which do not produce byproduct S.

Critical Data Gaps and Poorly Understood Phenomena

Included in the information gap is the exact char cost, raw material consumption, and the utility requirements. Also, the removal efficiencies of both NO_x and SO_x need to be established for various inlet gas compositions and operating conditions. The interference, if any, from any other gas species and the maximum tolerable flue gas particulate loading need to be determined. The manpower requirements are also unknown.

Advantages and Disadvantages

The advantages and disadvantages of the FW-BF adsorption process are listed below.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >95% SO_2 removal efficiency
3. Produces marketable byproduct (S)
4. Has been tested on coal-fired flue gas on pilot-plant or greater scale
5. Operates between 100 and 200°C (in adsorber) which may require negligible reheat

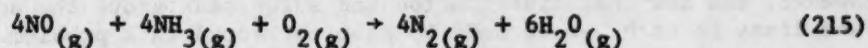
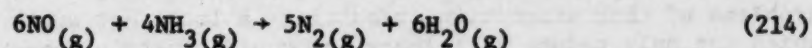
Disadvantages

1. Can only achieve a maximum NO_x removal efficiency of <70%
2. Forms secondary source of pollution (ash waste stream)
3. Requires significant amounts of energy for the regeneration step
4. Requires somewhat particulate-free gas feed
5. Requires hot solids handling
6. Uses moving-bed reactor which increases maintenance and catalyst attrition

HITACHI, LTD., PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (2, 45, 50, 51)

Hitachi, Ltd., has developed a dry, SCR process for NO_x removal. NH₃ is the reduction agent; information describing the catalyst composition has not been released. According to Hitachi, NO_x in the flue gas is decomposed into N₂ and H₂O by the following reactions at a temperature range of 250-400°C (482-752°F):



Hitachi recommends two methods of applying their NO_x removal process to treatment of flue gases which have a very low particulate level. In the direct method, the flue gas at about 300-400°C (572-752°F) from a hot ESP is injected with NH₃ gas before it enters the reactor. This flow scheme is shown in Figure 49. The gas is distributed in the fixed-bed reactor and passes through the catalyst layers where the NO_x reacts with the NH₃. The flue gas leaving the reactor enters the boiler air heater to heat incoming air to the boiler. The flue gas then passes through a desulfurization system before being emitted at the stack. In the original concept by Hitachi, the ESP was located after the air heater; however, its application was for oil-fired boilers. If the same method was used for coal-fired boiler application, the above scheme using a hot ESP would be necessary.

The second method uses a reheating scheme in which the flue gas is treated after desulfurization. The flue gas is heated from about 60°C (140°F) at the FGD outlet by passage through a heat exchanger and inline heater to the reaction temperature (300-400°C). NH₃ is injected into the gas as it passes from the heater to the fixed-bed reactor. Upon exiting the reactor, the treated gas passes through the heat exchanger to heat the incoming, untreated gas and then exits the stack.

The operating conditions which are applicable for the treatment of flue gas from the combustion of heavy oil are as follows:

Reaction temperature	300-400°C (572-752°F)
Space velocity	10,000-20,000 hr ⁻¹
NH ₃ :NO _x mol ratio	0.9:1-1.1:1
Pressure drop across the bed	100-150 mm H ₂ O
NO _x removal efficiency	>90%

Status of Development

Hitachi began working to find a catalyst for NO_x removal as early as 1963 for the treatment of automobile exhausts. This work was later succeeded by a project to develop an NO_x removal system and the associated catalysts

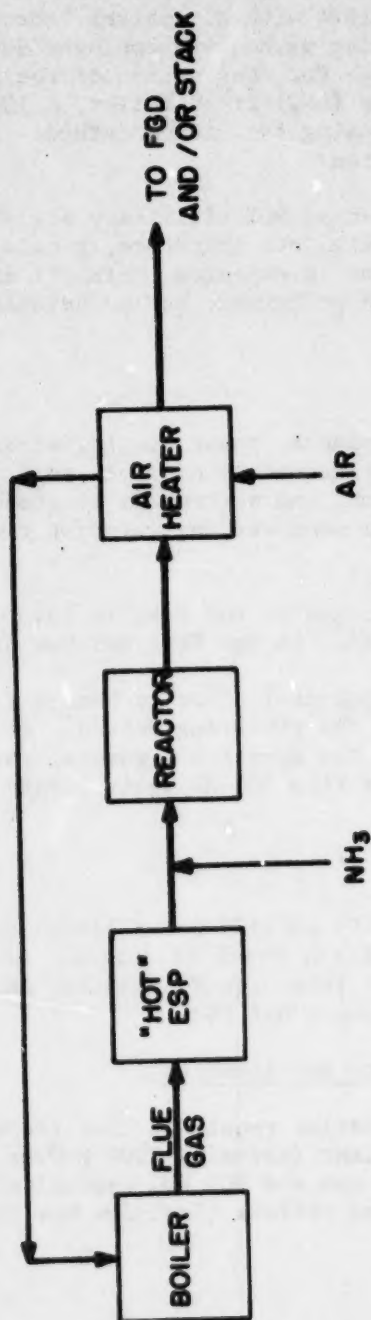


Figure 49. Flow Diagram of Hitachi, Ltd., Process.

for treatment of power plant flue gas. A 4000 Nm³/hr capacity pilot plant was constructed in 1974 using the direct method with crude heavy oil as the combustion fuel. This pilot plant was used to test catalyst life and to resolve potential scaleup problems and their solutions. A 200 Nm³/hr capacity bench-scale unit was operated in 1974 with Mitsubishi Petrochemicals to select the optimum catalyst. The reheating method was employed during these tests and the fuel source was heavy oil. For observation of the performance of the process on a liquefied natural gas (LNG)-fired boiler, a 1000 Nm³/hr capacity bench-scale unit started in 1975 using the direct method. Several other pilot plants have also been operated.

NO_x removal has been sustained at 90% efficiency for 7000 to 8000 hr with negligible deterioration of the catalyst; therefore, a catalyst life of at least 1 yr for commercial operation is expected. Hitachi states that tests with coal-fired flue gas have been performed, but no details have been released.

Background of Developer

Hitachi constructs chemical plants, power plants, steel plants, etc., and manufactures equipment for environmental control, such as ESP, desulfurization systems, NO_x removal systems, and wastewater treatment and waste disposal facilities. Hitachi also produces the catalyst for the NO_x removal systems.

The accessibility of this process to the U.S. is favorable since there are offices of Hitachi America, Ltd., in New York and San Francisco.

Hitachi has constructed a commercial plant to handle flue gas from a 170-MW equiv coke-oven plant with the reheating method. It was scheduled to begin operation in October 1976. Two direct NO_x removal facilities have been ordered each for treating flue gas from 700-MW equiv-plants with LNG-fired boilers.

Published Economic Data

The estimated capital cost (45) in 1976 for a 333-MW coal-fired plant (assuming 3000 Nm³/hr = 1 MW) is \$15M, which is \$45/kW. This is based on an NO_x removal efficiency of 90% with inlet gas NO_x content of 200 ppm. The site is Japan and this cost includes a hot ESP.

Raw Material, Energy, and Operation Requirements

NH₃ is the only major raw material required. For treating flue gas from a coal-fired boiler on a 333-MW plant (assuming 3000 Nm³/hr = 1 MW) with an inlet flue gas NO_x content of 200 ppm and 90% NO_x removal efficiency, the NH₃ and utility requirements are as follows (includes hot ESP):

<u>Material</u>	<u>Quantity</u>
NH ₃	4.2 short tons/day
Electricity	6000 kW
Steam	52.8 tons/day

The electrical requirement represents 1.8% of the total power output of the plant.

No maintenance, labor, or technical requirements are yet available.

Technical Considerations

This process is very simple as compared to wet processes. Process control should include automatic control of the NH₃ flow rate. Hitachi claims there are no effects on the catalyst with changes in NO_x inlet concentration and that the catalyst is free from adverse effects of SO₂.

With one of the largest space velocities of any dry process of 10,000 hr⁻¹ or greater and a typical reaction temperature for most dry NO_x removal facilities of 300-400°C (572-752°F), the reactor size should be about the same or slightly smaller than for other dry systems.

For retrofit application on a system with a cold ESP, the reheating method for NO_x removal would be required. Thus, an inline heater and heat exchanger would be necessary. If an FGD unit is also present, some energy saving in reheat could be realized by treating the gas between the ESP and FGD unit.

Since several NO_x removal trains are necessary for treating gas from a 500-MW size plant, turndown capability is accomplished by removal of trains as necessary. The materials of construction required are not specified. There are no byproducts with this process.

Environmental Considerations

The sensitivities of NO_x removal on LNG and heavy oil combustion gases to space velocity and temperature are shown in Figures 50 and 51. The NO_x removal efficiency increases as the temperature increases from 300°C to 400°C (572-752°F) and decreases as the space velocity increases from 5,000 to 20,000 hr⁻¹. Figure 52 shows a characteristic relationship of mol ratio of NH₃:NO_x to NO_x removal efficiency.

The NO_x removal process of Hitachi does not remove any other pollutants. There is no waste disposal necessary and apparently no secondary pollution problem, since in some tests the NH₃ concentration at the reactor outlet was reported to be <5 ppm, even with a space velocity of 20,000 hr⁻¹.

There are no apparent work hazards.

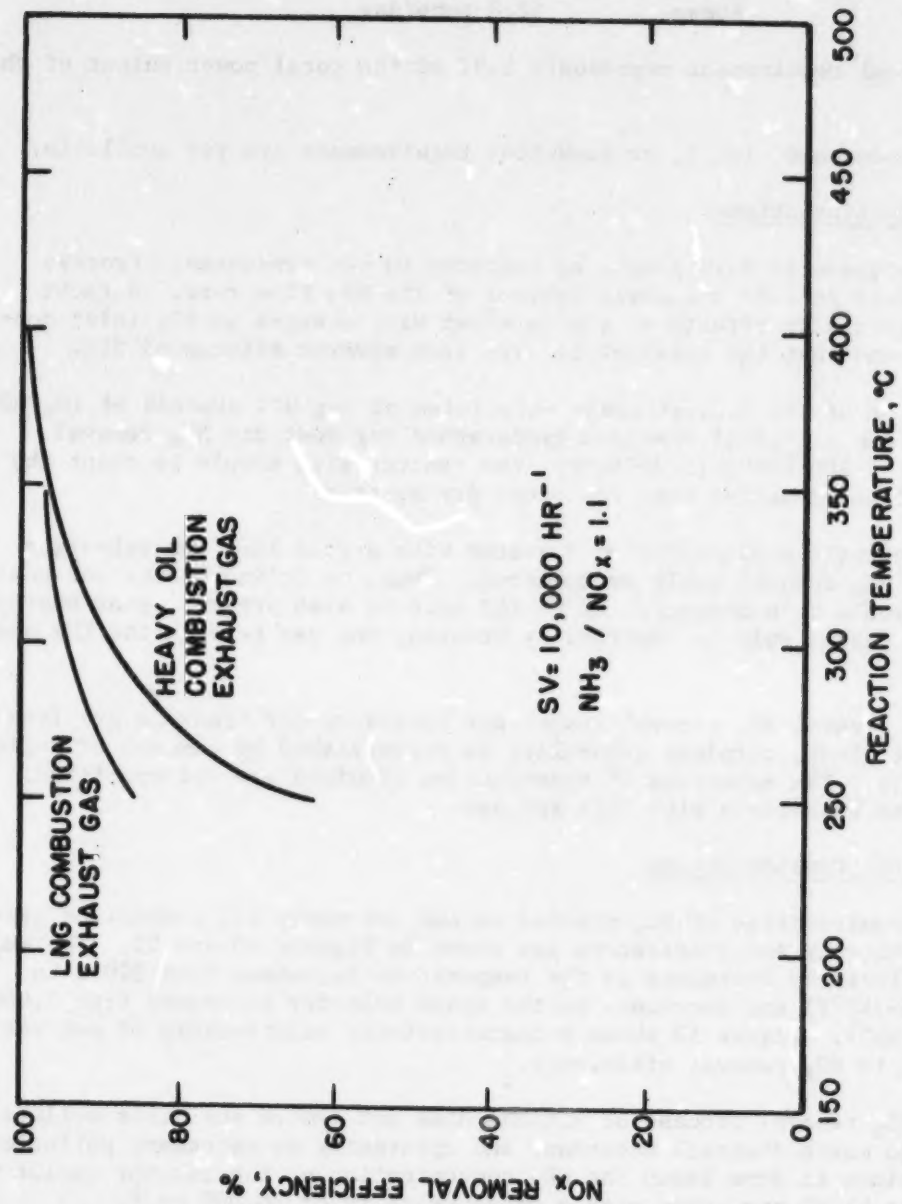


Figure 50. Relationship Between Reaction Temperatures and NO_x Removal Efficiency for Hitachi, Ltd., Process (50).

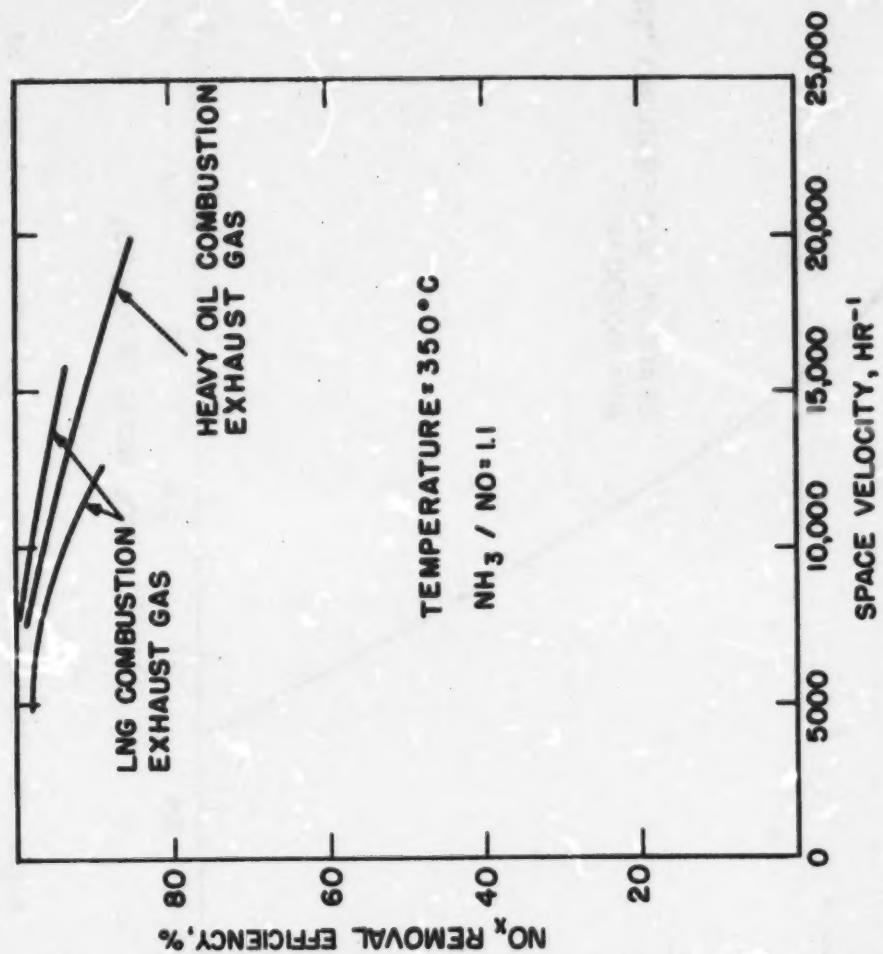


Figure 51. Relationship Between Space Velocity and NO_x Removal Efficiency for Hitachi, Ltd., Process (50).

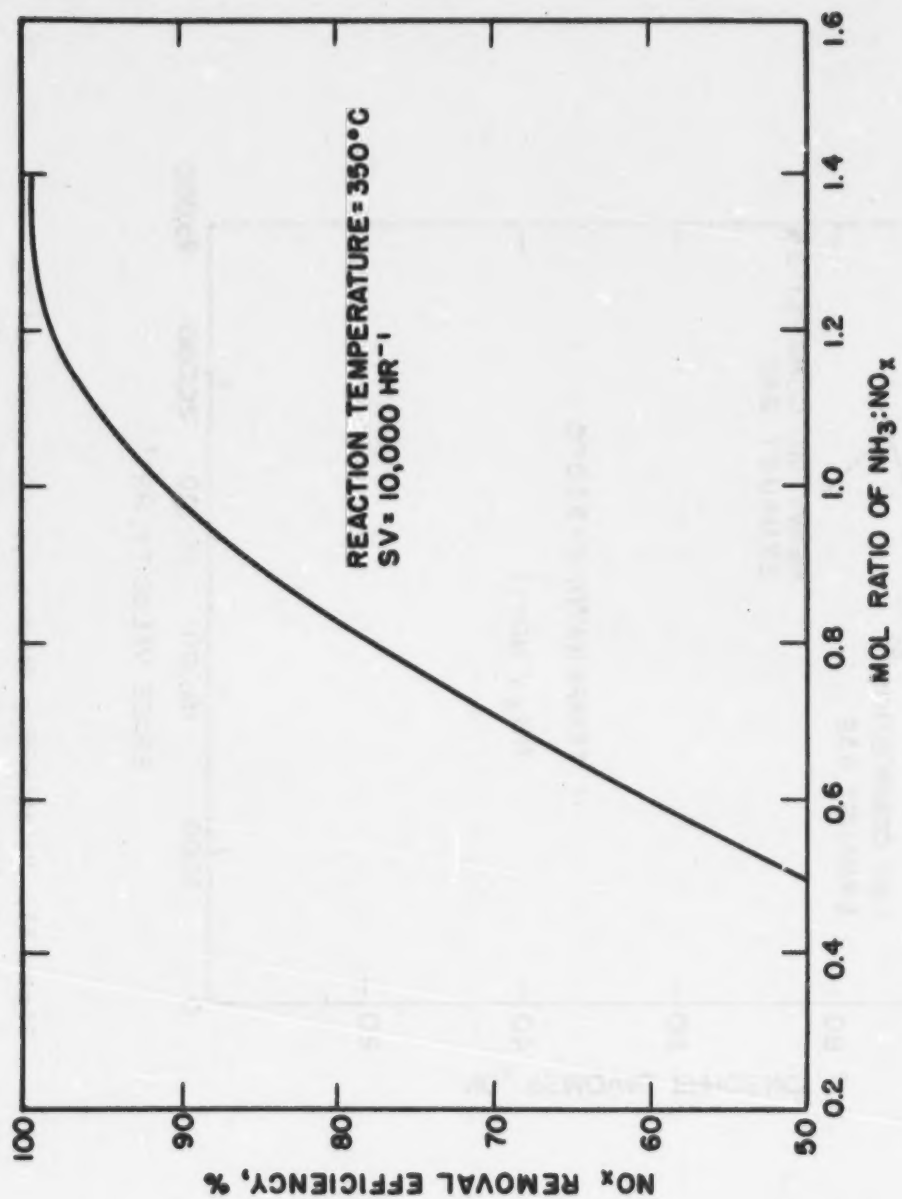


Figure 52. Characteristic Curve of the Effect of Mol Ratio of NH₃:NO_x on NO_x Removal Efficiency for Hitachi, Ltd., Process (51).

Critical Data Gaps and Poorly Understood Phenomena

Included in the data gap for the economics are the operating costs, though the capital investment required is given. The catalyst probably has a spherical or pellet structure; however, it has not been expressly stated. Also, the exact nature of the catalyst and the catalyst cost have not been released.

The maintenance and technical requirements are not known; however, they should be similar to most other dry NO_x removal processes. The major materials of construction are not available.

Other than for the economic and the raw materials and energy information reported herein, all the information has been from results on oil- or LNG-fired boilers. Hitachi states tests have been performed on coal-fired boilers, but details are not available.

Advantages and Disadvantages

Following are the advantages and disadvantages for the Hitachi process.

Advantages

1. Achieves >90% NO_x removal efficiency
2. Has been applied to flue gas from commercial coke-oven plant
3. Claims <10 ppm by vol NH_3 in treated flue gas

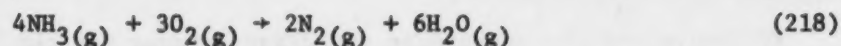
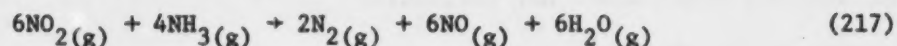
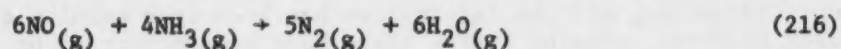
Disadvantages

1. Requires somewhat particulate-free gas feed

HITACHI ZOSEN PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (2, 4, 5, 10, 52, 58, 59)

Hitachi Zosen (Hitachi Shipbuilding and Engineering Company, Ltd.) has developed an NO_x removal process in which dry, SCR of NO_x with NH₃ occurs. Hitachi Zosen is now developing a catalyst and reactor design which permits treatment of flue gas with a high particulate loading. Therefore, the flue gas from a coal-fired boiler may be fed directly to the reactor, upstream to the air heater, without any particulate removal treatment as shown in Figure 53. Before entering the reactor, NH₃ is injected into the flue gas. In the reactor NO_x is reduced to N₂ by reaction with NH₃ in the presence of a catalyst and a temperature range of 300-400°C (572-752°F). The reactions occurring are listed by Hitachi Zosen as follows:



Reaction (218) represents the reaction of excess NH₃ with O₂ at 400°C to form N₂; therefore, Hitachi Zosen reports that no problem exists with excess NH₃ in the flue gas exiting the system. The treated flue gas passes to the air heater for heating the air feeding the boiler. After the treated flue gas is cooled in the heat exchanger, the gas is sent to the particulate removal and desulfurization steps before exiting the stack.

The NH₃:NO_x mol ratio employed is about (0.8-1.2):1. The reaction temperature range is 300-400°C (572-752°F) and Hitachi Zosen claims the pressure drop across the reactor is very low. The area velocity (flow rate of gas/surface area of catalyst) is between 7-10 Nm³/hr/m² and the relationship of catalyst surface area to bulk volume ranges from 550-600 m²/m³. The NO_x removal efficiency is >90%. The process is to be able to function with particulate loading up to 16 g/Nm³ (about 7 gr/sft³), making it possible to use this system before an ESP or particulate scrubber on flue gas from a coal-fired boiler.

The catalyst is manufactured into the shape of honeycomb units. These units are welded together for the particular size required. The flue gas passes parallel to the catalyst surface. The catalyst composition has not been revealed for proprietary reasons; however, Hitachi Zosen does state that it is constructed of common material. The expected catalyst life is reported to be 1 yr.

Status of Development

Hitachi Zosen has been developing an NO_x removal process and catalyst since 1970. Five different catalyst series have been created and are known as NOXNON 100, 200, 300, 400, and 500 series. The 100 series is nonselective

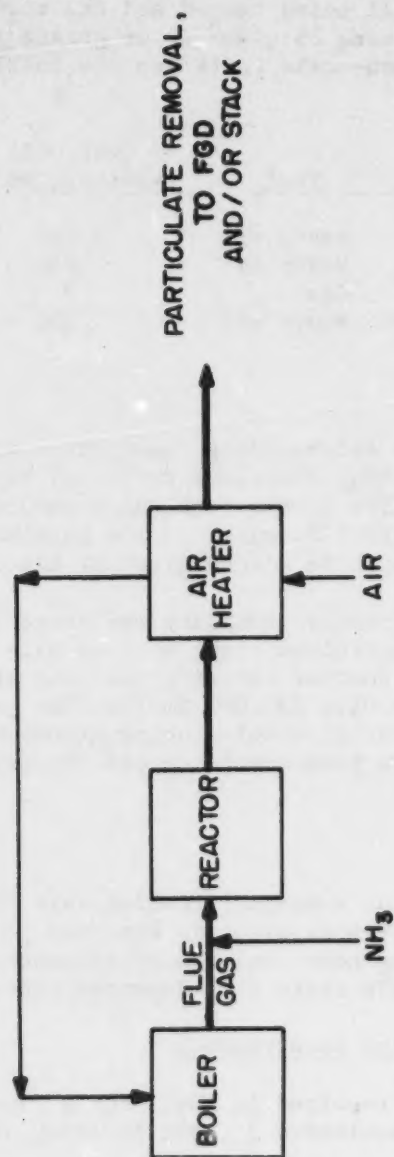


Figure 53. Flow Diagram of Hitachi Zosen Process.

and for use with CO, H₂, and hydrocarbons as reductants. The other four series are for use with NH₃ as the reducing agent. Series 200 is for treating "clean" flue gas, that is, gas which does not contain any significant amount of SO_x or particulates. The 300 and 400 series are resistant to SO_x. The 500 series is for use in gas with considerable particulate loading. There have been over 21 different pilot-plant tests since 1973 in developing these catalysts. The 500 series is still being tested and the results to date have been promising even on gas containing 15 g/Nm³ (6.44 gr/sft³) and 300 ppm SO_x. The following pilot-plant and bench-scale units are now testing the NOXNON 500 series catalyst.

Source of flue gas (plant type)	Fuel	Test unit capacity, Nm ³ /hr
Iron-ore sintering	Heavy oil	5,000
Iron-ore sintering	Heavy oil	200
Power	Coal	200
Glass-melting furnace	Heavy oil	200

Background of Process Developer

Hitachi Zosen is involved in shipbuilding, manufacturing of machinery, steel structures, and plants for NH₃, petroleum refining, and petrochemical products. There is a liaison office in New York which should improve the accessibility of the process to the U.S. market. The catalyst is manufactured by a chemical company in Japan which is a subsidiary of Hitachi Zosen.

A commercial-scale, SCR NO_x removal facility was constructed by Hitachi Zosen in the fall of 1975 for a petroleum plant with an oil-fired boiler and FGT capacity of 440,000 Nm³/hr. Another facility was completed in the fall of 1975 for a petroleum operation with 350,000 Nm³/hr flue gas capacity. Two more denitrification systems for steel manufacturing plants with 71,000 and 750,000 Nm³/hr flue gas rates have been completed and are reported to be operating successfully.

Published Economic Data

The estimated capital cost for a denitrification unit to treat flue gas containing 300 ppm NO_x on a 250-MW-size plant is reported to be about \$16/kW (58). The corresponding operating cost would be approximately 1.5 mills/kWh (59). These are assumed to be 1976 costs at a Japanese site.

Raw Material, Energy, and Operation Requirements

The only major raw material required is NH₃. For a 250-MW plant with 300 ppm NO_x in the flue gas, an estimated 5 short tons/day of NH₃ is required for NO_x removal.

On the same basis as above, the following energy consumption for denitrification is required:

<u>Energy</u>	<u>Quantity</u>
Electricity	400 kW
Steam	4.1 tons/day

No reheat fuel is necessary. The electrical requirement represents 0.2% of the total power output of the plant. The majority of the steam (2.9 tons/day) is used for NH_3 vaporization, while the remaining 1.2 tons/day is for soot blowing.

With no particulate scrubbing before the NO_x removal system, soot blowing of the air heater and the reactor are required. For pilot plants, the reactor has required washing out of deposits once every 2 mo and Hitachi Zosen states that this operation requires only a few min to complete. The technical support necessary for operation of this NO_x removal system should be similar to other dry systems.

Technical Considerations

Having only the reactor and NH_3 storage and injection system, this process would be a direct and simple dry process. Process control would include automatic control of NH_3 flow rate. On a recently constructed plant, the NH_3 flow rate is automatically controlled based on the total inlet gas flow rate and inlet NO_x concentrations.

There is no information available yet on the sensitivity of the process to inlet gas composition.

The equipment size for this system should be comparable to other dry NO_x removal systems. The reaction temperature is similar at 300–400°C (572–752°F) and the area velocity range is comparable at 7–10 $\text{Nm}^3/\text{hr}/\text{m}^2$.

In retrofit application, it would be most advantageous to treat the flue gas for NO_x removal prior to the air heater whether or not an FGD system or only a cold ESP is present. More energy would be required to reheat the flue gas to reaction temperature if the gas is treated after the air heater and even more energy is required if the FGD system is located before the NO_x removal system. The Hitachi Zosen process would have the advantage over other processes of less area required since there are fewer pieces of equipment. The turndown capability of this process is similar to other dry systems in that an NO_x removal train could be removed from service.

The major material of construction is reported to be carbon steel.

There is no byproduct made in this process.

Should future results prove this direct FGT infeasible, Hitachi Zosen has a more conventional NO_x removal process, such as found on the commercial plants constructed by Hitachi Zosen for oil-fired boilers. It employs the heat exchanger, heater, and particulate removal discussed in the other dry NO_x removal processes and is comparable to other processes. The estimated capital cost for this system is estimated to be \$50–\$60/kW based on 40–150

ppm NO_x, 1976 costs, and 300 yen/\$. The NO_x removal efficiency is reported to be >90% and operating conditions are similar to those previously reported. The operating cost is estimated at 3.3 mills/kWh.

Environmental Considerations

Little information has been reported on the sensitivity of NO_x removal efficiency to various operating conditions. The only data available indicate the NO_x removal efficiency approaching 90-100% at 350°C (662°F) and above for most of the catalysts. The efficiency drops off to 60-70% at 300°C (572°F).

There are no additional pollutants removed, other than NO_x, by the Hitachi Zosen process.

Excess NH₃ at the outlet of the system is a potential problem; however, Hitachi Zosen claims NH₃ exiting the system is very low and creates no pollution problem. Some type of disposal for the reactor deposit washing solution would be essential. Also, the catalyst is disposed of and not reclaimed.

There are no apparent work hazards.

Critical Data Gaps and Poorly Understood Phenomena

There is no information available presently on the sensitivity of the NO_x removal efficiency to factors such as inlet gas composition and various operating conditions. Specifically, there is no comment on any possible adverse effects from Cl⁻ in the flue gas from a coal-fired boiler. These effects might include interference of NO_x removal efficiency or deterioration of catalyst.

The composition of the catalyst is not known. The exact cost per pound is not known though the estimated cost for the initial investment in catalyst necessary for a 250-MW plant with flue gas containing 300 ppm NO_x is given by Hitachi Zosen as \$1.7M (1976 cost and assuming 300 yen = \$1).

There are few available facts on wash frequency and other washing requirements on the reactor treating the flue gas directly from a coal-fired boiler with no particulate removal. More information should be accessible as the pilot-plant tests progress.

Maintenance, operating, and technical support requirements have not been published.

Advantages and Disadvantages

Advantages

1. Achieves >90% NO_x removal efficiency
2. Has been applied to flue gas from commercial oil-fired boilers
3. Operates with full particulate loadings (>7 gr/sft³)
4. Is probably <10 ppm by vol NH₃ in treated flue gas

Disadvantages

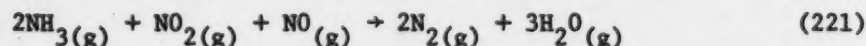
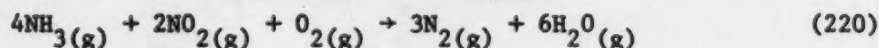
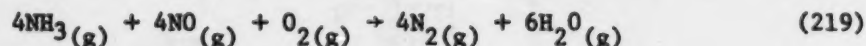
None is readily apparent now.

JGC PARANOX PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (2, 4, 9, 62, 63, 64, 96)

JGC Corporation's "Paranox" process removes NO_x from flue gas by SCR employing NH₃ as the reducing agent. The catalyst was developed by JGC and a parallel-passage reactor is applied.

The flow diagram for the Paranox process is shown in Figure 54 and, excluding the ESP assumed necessary for coal-fired flue gas, it is the same as for the treatment plant at the Kashima Refinery of Kashima Oil. Flue gas from a coal-fired boiler would pass through an air heater for heat recovery to air feeding the boiler and then an ESP for particulate removal. The flue gas then is heated to 380-420°C (716-788°F) by passage through a counter-current heat exchanger and an auxiliary heater. NH₃ is injected into the flue gas before it enters the parallel-passage reactor. The main chemical reactions in the reactor by which NO_x is converted to N₂ and H₂O by reduction with NH₃ are stated by JGC to be as follows:



After exiting the reactor, the flue gas passes through the countercurrent heat exchanger to heat the incoming, untreated gas passing to the reactor. After exiting the heat exchanger, the treated flue gas passes to a desulfurization unit and/or the stack.

The operating conditions at the Kashima plant are as follows:

Reactor temperature	380-420°C (716-788°F)
NH ₃ :NO _x mol ratio	(1.1-1.3):1
Pressure drop (see Figure 55)	180-200 mm H ₂ O
Particulate loading	0.05 g/Nm ³ (0.02 gr/sft ³)

The NH₃ injected into the flue gas has been diluted with steam at a steam to NH₃ mol ratio of 20:1. A stable NO_x removal efficiency of >95% has been demonstrated with an inlet gas NO_x concentration of 60-250 ppm. The concentration of NH₃ exiting in the treated gas is reported to be <10 ppm. The catalyst life is expected to be at least 1 yr.

Status of Development

The Paranox process consists of a denitrification catalyst, developed by JGC, and the parallel-passage-type reactor, developed by Shell and patent rights possessed by Shell International Petroleum Maatichappij (SIPM). Nihon Shell Gijutsu KK, a joint undertaking created by Shell Kosan Company and JGC, is the licensing agent for the Paranox process in the Far East.

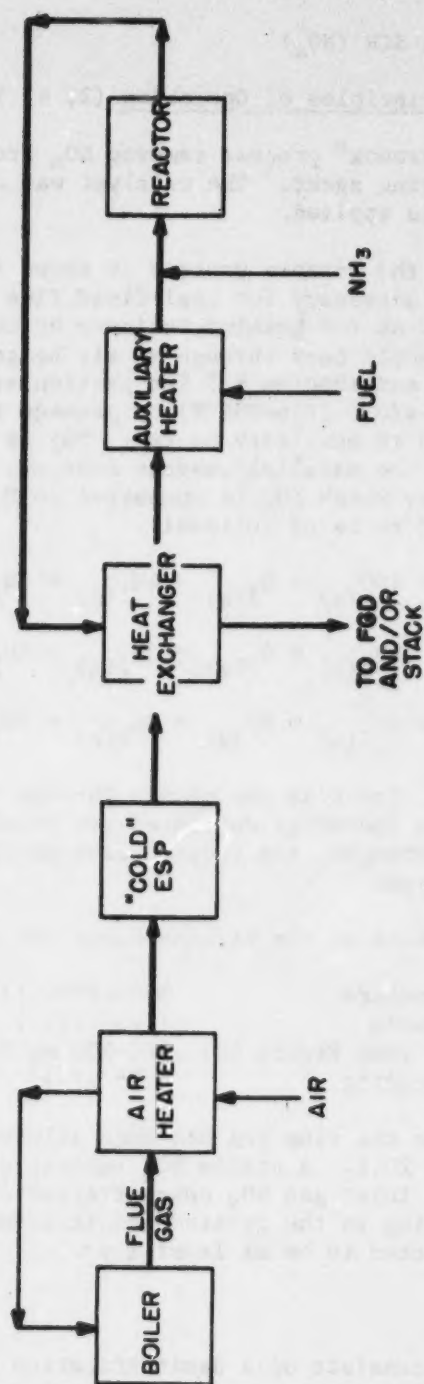


Figure 54. Flow Diagram of JGC Paranox Process.

Background of Process Developer

JGC Corporation, formerly Japan Gasoline Company, Ltd., is an engineering and plant construction organization offering services in engineering, consulting, procurement, construction, and operation management. The fields of activity encompass petroleum, petrochemical, and diversified gas projects, environmental conservation, nuclear projects, desalination, foods, and pharmaceuticals. JGC built the Shell FGD unit at Showa Yokkaichi Sekiyo and has developed its own catalyst for SCR of NO_x . It has constructed two prototype units. One is at Kashima Refinery for Kashima Oil with a flue gas treating capacity of $50,000 \text{ Nm}^3/\text{hr}$ and it has operated since November 1975. The second is a $70,000 \text{ Nm}^3/\text{hr}$ capacity treatment plant for Fuji Oil. The Paranox process may not be as accessible to the U.S. market as other processes since no contact could be made with any JGC Corporation office in the U.S.

Published Economic Data

The capital cost for a $150,000 \text{ Nm}^3/\text{hr}$ gas treatment facility with 85-90% NO_x removal is estimated to be \$1.33M, which is about \$27/kW (96). Values for operating costs have not been reported. The above estimate was for oil-fired gas treatment and does not include an ESP and is assumed to be 1976 values for a Japanese location.

Raw Material, Energy, and Operation Requirements

The major raw material is NH_3 and for an $\text{NH}_3:\text{NO}_x$ ratio of 1.2:1, it is estimated that 24 short tons of NH_3 /day are required for a 500-MW equiv plant with an inlet flue gas containing 600 ppm NO_x . Fuel and electricity are the major energy sources required and no estimates for their usage are available. The manpower and technical requirements are not stated, but are expected to be the same as similar dry processes.

Technical Considerations

The Paranox process involves simple and straightforward chemistry. The NH_3 flow rate and reaction temperature should be capable of being automatically controlled. The information obtained on NO_x removal sensitivity to inlet gas concentration is shown in Figures 55-58. In Figure 55 NO_x in the inlet gas ranges from 90-100 ppm while the outlet gas consists of 1-3 ppm NO_x . NO_x removal results with varying inlet NO concentrations are shown in Figure 56 while the effects of different O_2 and H_2O levels in the flue gas on NO_x removal efficiency are displayed in Figures 57 and 58 respectively.

The space velocity is not specified, but if in the $4000\text{-}7000 \text{ hr}^{-1}$ range, the equipment size necessary will be comparable to that of most other dry processes with similar reaction temperatures.

The Paranox process is suitable for retrofit on a plant with a cold ESP and with or without an FGD unit. If placed after the FGD unit, more reheat will be required. For coal-fired flue gas, the Paranox process may be as

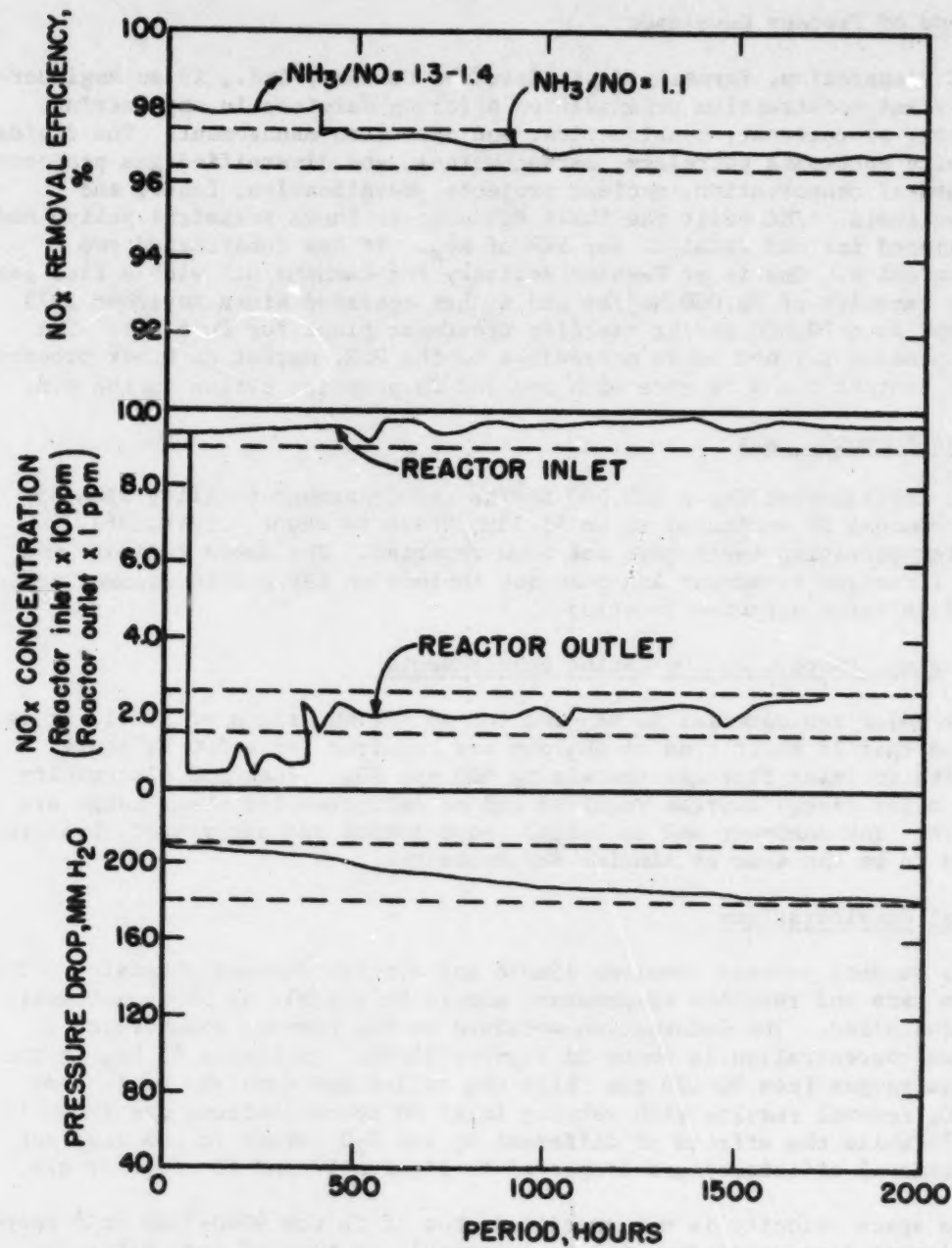


Figure 55. NO_x Removal Efficiency, NO_x Concentration, and Pressure Loss Over 2,000 hr Test Period for JGC Paradox Process (2).

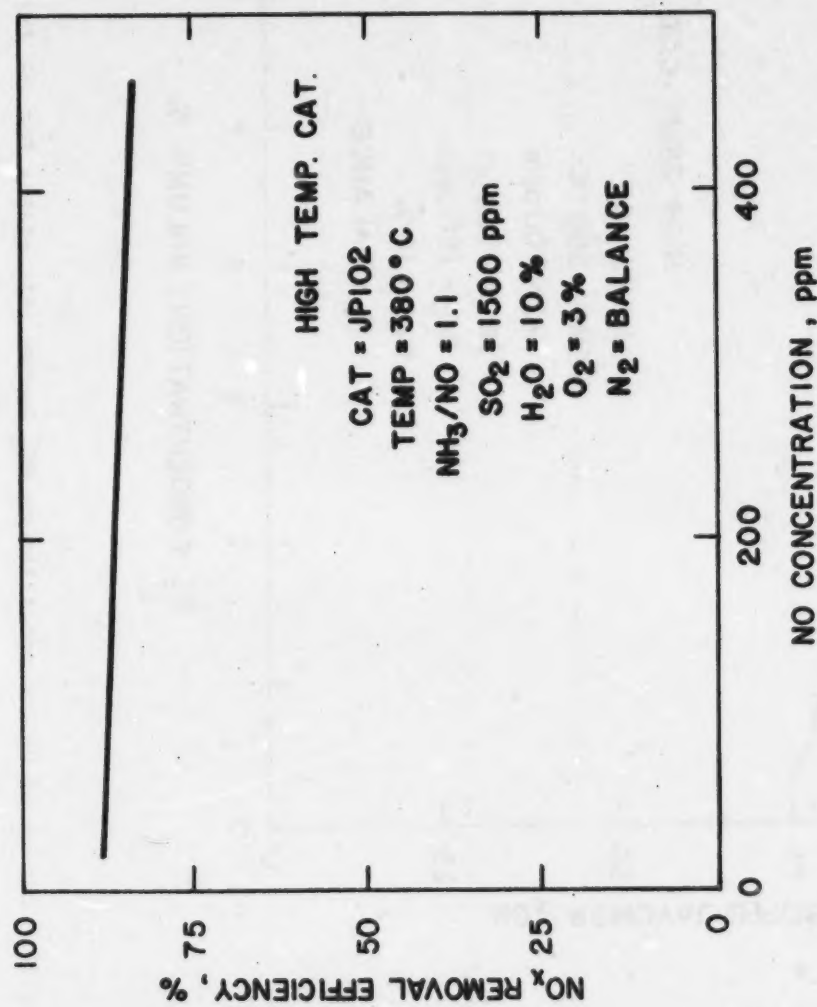


Figure 56. Effect of NO Initial Concentration on NO_x Removal Efficiency for JGC Paradox Process.

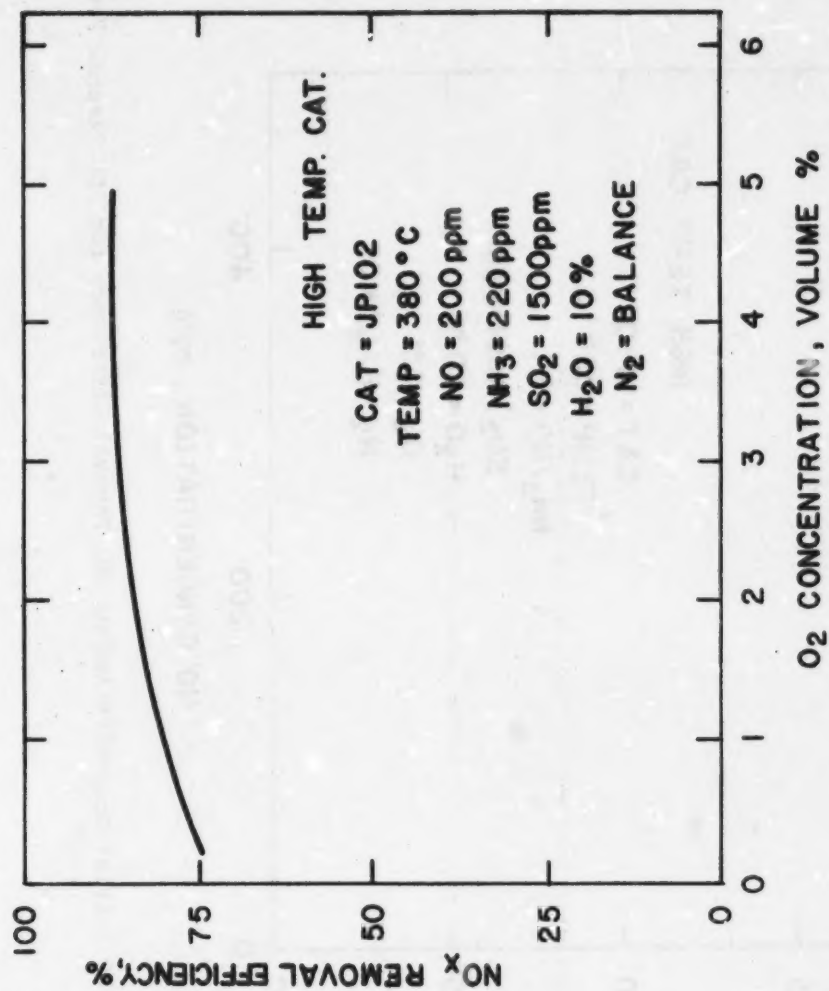


Figure 57. Effect of O₂ Concentration on NO_x Removal Efficiency for JGC Paradox Process (64).

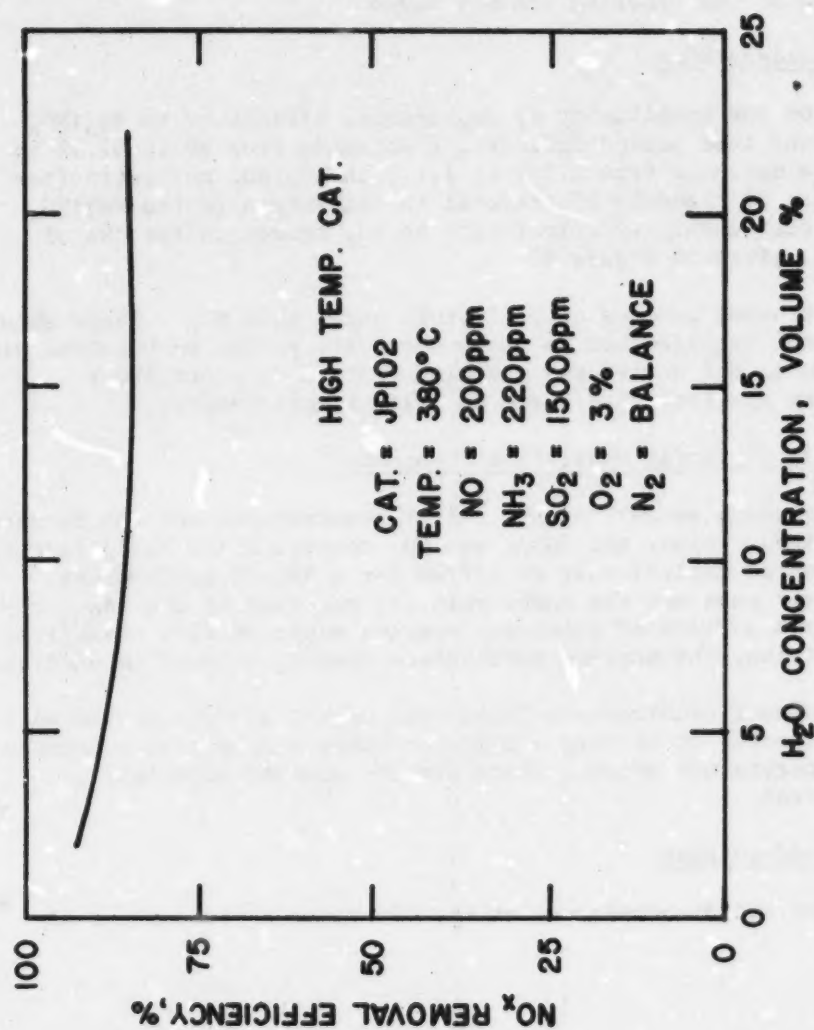


Figure 58. Effect of H₂O Concentration on NO_x Removal Efficiency for JGC Paranox Process (64).

suitable as some other dry processes mentioned for treating the flue gas before the air heater. Savings in fuel for reheat would be significant and elimination of the heat exchanger would also result. Of course, a hot ESP with larger power consumption would be required.

Several NO_x removal trains would be required for treating a 500-MW equiv-gas stream. Therefore, as for other dry processes, the major turndown capability would be the removal of a train from the process. The auxiliary heater would provide temperature control during boiler load fluctuations.

The materials of construction are not known.

Environmental Considerations

Information on the sensitivity of NO_x removal efficiency to $\text{NH}_3:\text{NO}_x$ ratio over a 2000-hr test period indicates a decrease from 99 to 97.5% in NO_x removal with a decrease from 1.3:1 to 1.1:1 in $\text{NH}_3:\text{NO}_x$ mol ratio (see Figure 55). Figure 59 presents NO_x removal in comparison to the $\text{NH}_3:\text{NO}_x$ mol ratio. The relationship of temperature to NO_x reduction for two of JGC's catalysts is given in Figure 60.

The Paranox process removes no pollutants other than NO_x . There should be no waste disposal required nor is there secondary pollution problems since the NH_3 is <10 ppm in the outlet gas. No information is known about interference of gas species. There are no evident work hazards.

Critical Data Gaps and Poorly Understood Phenomena

The operating costs as well as the energy requirements for the Paranox process are not given. Also, the inlet gas NO_x concentration basis is not known for the reported capital cost of \$27/kW for a 500-MW equiv-plant. Included in the data gaps are the space velocity required in the reactor and the possible adverse effects of other gas species expected with coal-fired flue gas. In addition, the maximum particulate loading allowed is uncertain.

The exact manpower requirements (labor and technical) are not known though they are expected to be very similar to other simple, dry processes. It has not been ascertained whether there are any unusual materials of construction required.

Advantages and Disadvantages

The advantages and disadvantages of the JGC Paranox process are as follows:

Advantages

1. Achieves >90% NO_x removal efficiency
2. Claims <10 ppm by vol NH_3 in treated flue gas

Disadvantages

1. Has not been tested on coal-fired flue gas
2. Requires, apparently, somewhat particulate-free gas feed
3. Requires auxiliary heater to attain or control reaction temperatures

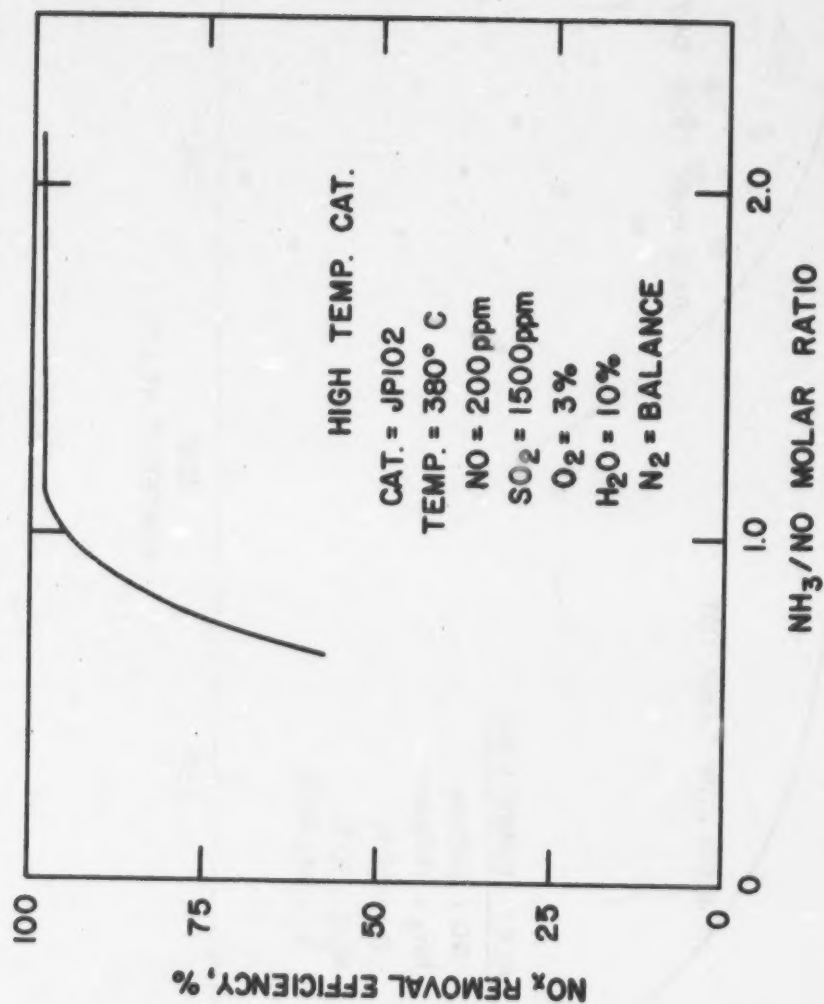


Figure 59. Effect of NH₃:NO Mol Ratio on NO_x Removal Efficiency for JGC Paradox Process (64).

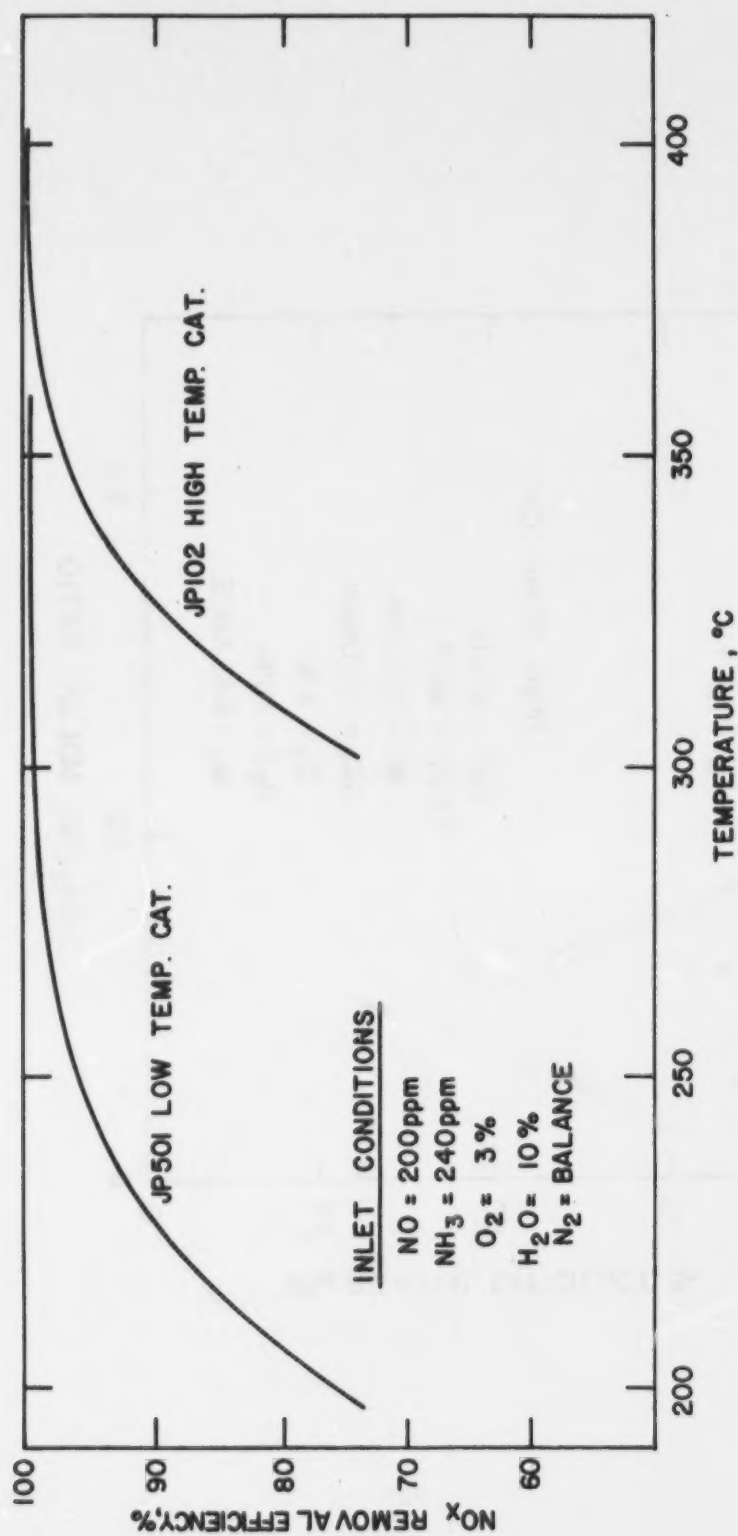


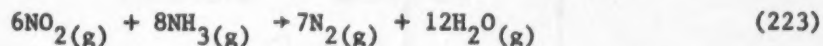
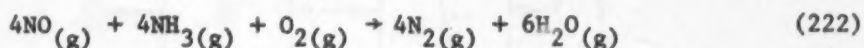
Figure 60. Effect of Temperature on NO_x Removal Efficiency for JGC Paradox Process (64).

KOBE STEEL PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (69, 70)

The Kobe Steel process is a dry NO_x-only removal system based on the SCR of NO_x using NH₃. This dry NO_x process is similar to the other dry processes since it consists of three distinct sections: particulate removal, NH₃ injection, and catalytic reduction, as shown in the flowsheet in Figure 61. Kobe Steel has developed two different types of reduction reactors, one for "clean" flue gas and one for particulate-laden gases, the latter of which will be the only one considered in this description.

The flue gas from the boiler at 350-400°C (660-750°F) passes through a hot ESP to reduce the particulate levels below 0.2-0.4 g/Nm³ (0.09-0.17 gr/sft³ at 32°F) and enters a mixing chamber where gaseous NH₃, in an NH₃:NO_x mol ratio of (1.0-1.1):1, is intimately mixed with the flue gas before entering the KSL moving-bed reactor. As the mixture of flue gas and NH₃ pass over and through the moving packed-bed sections containing the proprietary base-metal catalyst, NO_x is selectively reduced to N₂ by the following reactions:



Since most of the NO_x in the flue gas is present as NO, reaction (222) is the primary reaction occurring in the reduction reactor. The clean flue gas from the reactor passes through the air heater and then an FGD section before exiting through the stack.

Status of Development

Two bench-scale units using the Kobe Steel KSL moving-bed process to treat 1000 Nm³/hr (0.3 MW equiv) of "dirty" flue gas was started up recently and testing of the process on dirty flue gas (30-150 ppm SO₂, 300-400 ppm NO_x, 0.2-0.4 g/Nm³ of dust) is apparently continuing at the present time. The longest period of continuous operation was 8000 hr (330 days) during a test of the catalyst's life expectancy in particulate-laden flue gases.

Although this process has not been tested on coal-fired flue gas, the Kobe Steel process should be able to adjust to the higher particulate and NO_x levels associated with coal-fired flue gas since it has been tested on flue gas from a coke plant and a pelletizing plant containing approximately 0.2-0.4 g/Nm³ of dust and 300-400 ppm NO_x.

The next development step for this process would be the continuation of current testing in the 1000 Nm³/hr bench-scale units to generate data on raw material, energy, and catalyst consumption. In addition, the ability of the Kobe Steel process to handle the flue gas from a coal-fired boiler needs to be demonstrated during long-term continuous pilot-plant operation.

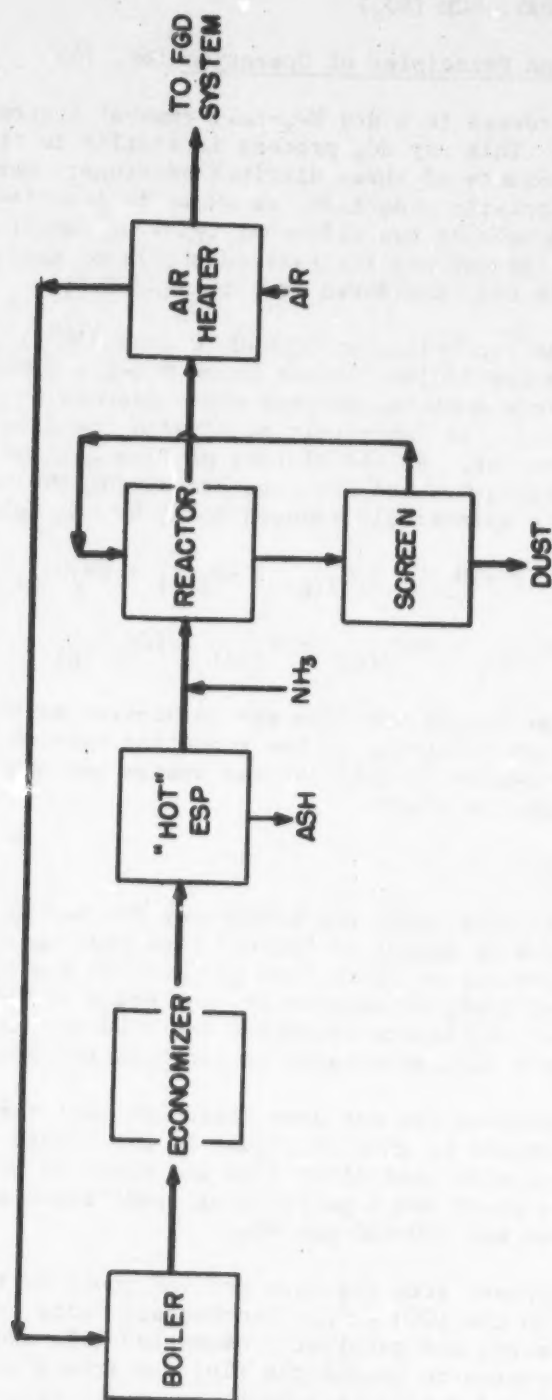


Figure 61. Flow Diagram of Kobe Steel Process.

Background of Process Developer

Kobe Steel, Ltd., is a large Japanese corporation heavily involved in the iron and steel industry. With the coming of the strict air pollution regulations in Japan in the early 1970's, Kobe Steel entered the air pollution control field to solve the SO_2 emissions problems from their plants. Their CaL-SO_x wet limestone FGD system (KSL FGD process) was developed and has reached the commercial operation stage. In response to increasingly strict NO_x levels, Kobe Steel began the development of both a dry SCR process using NH_3 and also a wet absorption-oxidation process. The development of this wet absorption-oxidation has recently been suspended and the development of a new wet process has been initiated. Their dry SCR process was split into two types, one to treat clean gas and one to treat dirty flue gas, with the only major difference being the design and type of reduction reactor.

At the present time no American company has been licensed to market this technology in the U.S. However, Kobe Steel does have a liaison office in New York City through which inquiries about this process are handled.

Published Economic Data

Based on the premises of a 500-MW coal-fired boiler and 600 ppm NO_x in the inlet flue gas, the capital investment for the Kobe Steel process has been estimated (43) as \$4-7 Nm^3/hr of flue gas. This value corresponds to \$12-21/kW of installed capacity (construction basis: Japan and 1976 dollars). The annual operating cost is expected to be \$3-4 Nm^3/yr of flue gas, which, assuming 7000 operating hr/yr, is equivalent to about 1.3-1.7 mills/kWh (43).

Raw Material, Energy, and Operation Requirements

The only major raw material requirement for this process would be NH_3 with some makeup catalyst required to replace losses due to attrition. The only major energy requirement would be electricity. No information has been published yet on the quantities of NH_3 , catalyst makeup, or electricity required for this process.

In addition, the operating manpower and maintenance requirements have also not been made available. Kobe Steel does state that the process is fully automated and what little operating adjustments which are required can be handled by personnel from other areas of the power plant.

Technical Considerations

The Kobe Steel flue gas denitrification process is a relatively simple unit with only five pieces of equipment: a hot ESP, an NH_3 storage tank, an NH_3 vaporizing unit, a mixing vessel, and a reduction reactor. The only major process control problem is vaporizing and injecting the exact amount of NH_3 required to provide an $\text{NH}_3:\text{NO}_x$ mol ratio of (1.0-1.1):1 in

the reduction reactor. Although the exact control mechanism has not been specified by Kobe Steel, the NH_3 is probably metered into the mixing tank in direct proportion to the amount of flue gas passing through the system.

The KSL moving-bed reactor will be the largest and most complex piece of equipment in this system and a diagram of this reactor is shown in Figure 62. The catalyst pellets enter the reactor from the top and gradually drop to the bottom of the reactor beds as they become clogged with particulates from the flue gas. Although the residence time and pellet size for the base-metal catalyst have not been specified by Kobe Steel, from the numerous graphs provided it is estimated for 90% NO_x removal, the smaller catalyst size 3-7 mm (0.1-0.3 in.) in diameter will be required to obtain a reasonable space velocity through the reactor. The use of the smaller catalyst pellets, however, will sharply increase the pressure drop through the reactor during routine operation and increase the rate of catalyst movement through the bed. The higher velocity of the catalyst will, of course, result in larger catalyst losses due to increased breakage and also to larger maintenance costs.

For the purpose of this study then the operating condition in the reduction reactor would be the following:

Parameter	Value
$\text{NH}_3:\text{NO}_x$ mol ratio	(1.0-1.1):1
Temperature	350°C (660°F)
Space velocity	10,000 hr^{-1}
Catalyst size (shape)	3-7 mm dia (pellet)
Maximum tolerable dust level	0.2-0.4 g/ Nm^3

These operating parameters for the reduction reactor in the Kobe Steel process are very similar to those given for the other SCR processes.

The NO_x removal efficiency is relatively independent of the flue gas composition, excluding particulate levels, under normal circumstances. As long as the temperature in the reactor remains near the recommended operating temperature of 350°C the denitrification efficiency is insensitive to the SO_2 concentration. The NO_x removal efficiency is completely independent of the H_2O , O_2 , and NO concentrations in the flue gas, providing that the O_2 concentration is 1% or greater. The particulate levels must remain below 0.2-0.4 g/ Nm^3 to prevent excessive plugging in the reactor.

This process could not be easily retrofitted onto an existing 500-MW plant equipped with cold ESP. The ductwork modifications required to remove and return the flue gas between the economizer and the air heater would be extremely difficult and expensive. Thus for retrofit applications the flue gas would be removed after the existing cold ESP and sent to a countercurrent heat exchanger where the raw flue gas extracts waste heat from the clean flue gas exiting the denitrification section. The flue gas is further heated in an oil-fired furnace to raise the temperature of 350°C (660°F) and then mixed with gaseous NH_3 before entering the reduction reactor. As the gas

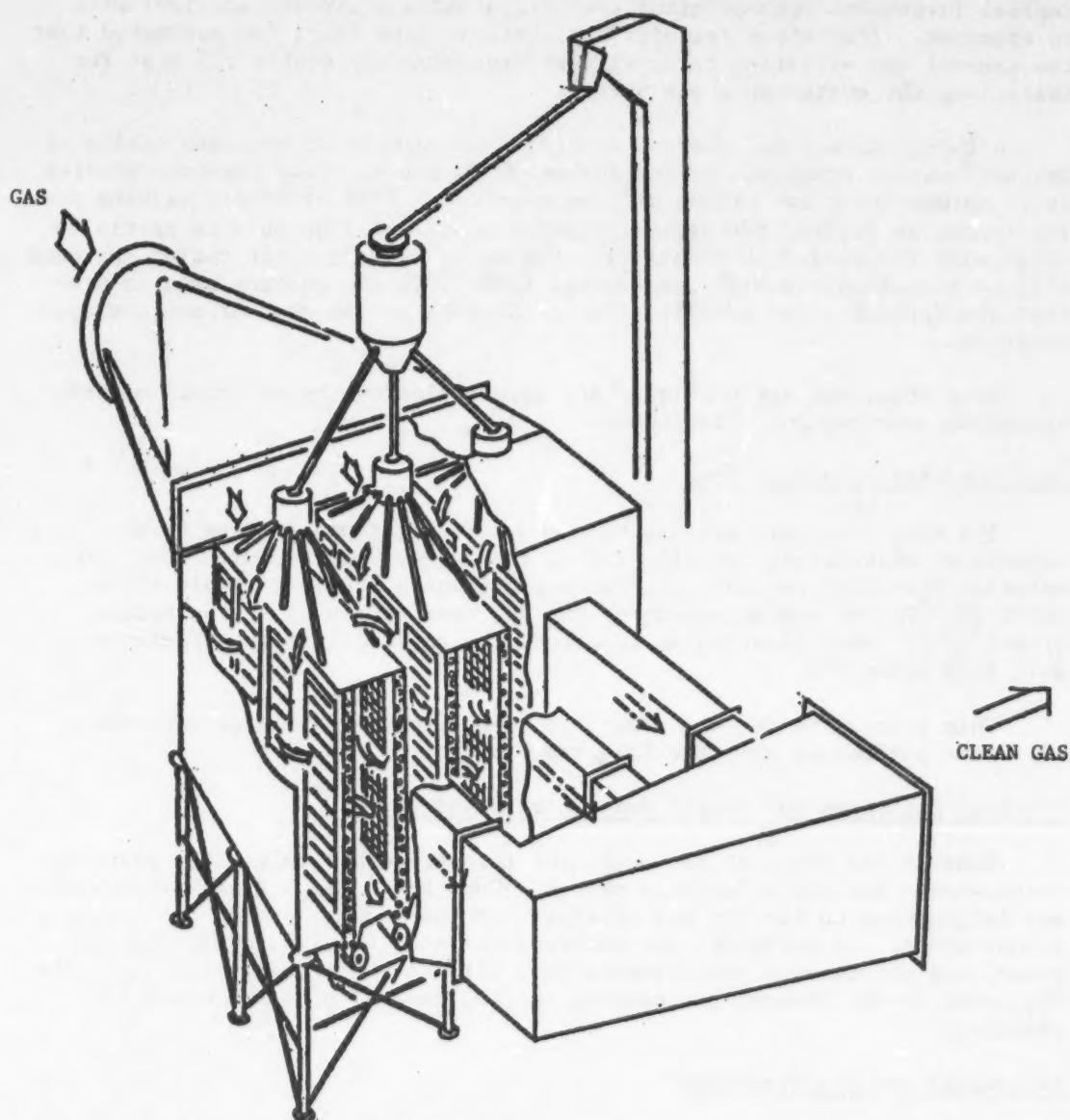


Figure 62. Catalyst Reactor of KSL Moving Bed (70).

mixture passes through the reactor, the NO_x is catalytically reduced to N_2 and the effluent gas is sent to the heat exchanger to preheat the incoming raw flue gas before entering the desulfurization section. Thus, the retrofitting of this system on existing power plants will increase both the capital investment and operating cost since extra equipment and fuel will be required. (For these retrofit applications Kobe Steel has estimated that the capital and operating costs will be approximately double the cost for installing the system on a new unit.)

Although Kobe Steel has not disclosed the number of separate trains of denitrification equipment needed for a 500-MW boiler, from previous studies it is assumed that two trains will be required. Thus by simply closing down the trains as needed, the denitrification system will be able to partially cycle with the boiler availability. The major consideration during turndown will be to maintain a high temperature (350°C) in the reactor area to prevent the formation and precipitation of NH_4HSO_4 on the reactor and catalyst surfaces.

Kobe Steel has not published any information on the materials of construction required for this process.

Environmental Considerations

The Kobe Steel process has been shown in pilot-plant tests to be capable of selectively removing 90% of the NO_x by reaction with NH_3 . To maintain this high removal efficiency the temperature must remain above 350°C (660°F) and the mol ratio of $\text{NH}_3:\text{NO}_x$ must remain at approximately (1.0-1.1):1. When less NH_3 is injected, the denitrification efficiency will fall below 90%.

This process is for the selective removal of NO_x and does not remove any other pollutants from the flue gas.

Critical Data Gaps and Poorly Understood Phenomena

Many of the critical data gaps for this process involve the operating requirements and costs for this system. Kobe Steel has not as yet published any information on the NH_3 and catalytic consumption and cost, and energy requirements. In addition, the materials of construction, operating manpower, and maintenance requirements have also not been made available. The NH_3 level in the treated gas exiting the NO_x removal system has not been reported.

Advantages and Disadvantages

The advantages and disadvantages for the Kobe Steel process are listed below:

Advantages

1. Achieves >90% NO_x removal efficiency

Disadvantages

1. Has not been tested on coal-fired flue gas
2. Has been tested only in a bench-scale unit
3. Requires somewhat clean (particulate level must be below about 0.1-0.2 gr/sft³) gas feed
4. Uses moving-bed reactor which increases maintenance and catalyst attrition

KURABO KNORCA PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (4, 5, 7, 68, 71, 73, 98)

Kurabo's NO_x removal process involves selective reduction of NO_x with NH₃ using Kurabo's own developed catalyst. Two catalysts and support systems have been developed by Kurabo. One is CuO on Al₂O₃ which was established first. The second system, composed of an iron (Fe) based catalyst on titanium dioxide (TiO₂) carrier, was just recently developed and would be more applicable to coal-fired FGT. The released information on this latter catalyst and support material is limited and thus the CuO catalyst with alumina support is used in this process description. The general removal principles are the same for either catalyst.

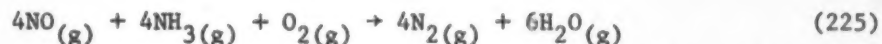
Based on the flow scheme of the 30,000 Nm³/hr capacity prototype unit for oil-fired FGT, an assumed process flow diagram for a coal-fired FGT operation is shown in Figure 63.

The gas from a coal-fired boiler, after having the particulates removed (e.g., by ESP), is sent to an auxiliary heater to (1) maintain the reactor temperature above 350°C (662°F), (2) prevent NH₄HSO₄ formation and depositing on the catalyst in the reactor, and (3) control reactor temperature with fluctuating boiler load. Kurabo states that this may not be necessary if the catalytic reactor can be located before the boiler-economizer or by-passing a portion of the superheater flue gas. Initially the flue gas is at 350°C (662°F) prior to the auxiliary heater, and the gas is at the optimum reaction temperature of 390-420°C (734-788°F) after the heater. NH₃ is injected into the gas between the heater and reactor. Kurabo states that SO₃ reacts with the CuO catalyst to form copper sulfate (CuSO₄). The CuSO₄ acts as a catalyst for the reduction of NO_x to N₂ by reaction with NH₃. The reactor has a moving catalyst bed. The spherical catalyst (3-5 mm dia) moves slowly downward continuously while the flue gas passes through the reactor in crossflow. The catalyst removed from the reactor has the dust removed, is reactivated (CuSO₄ → CuO) by heating to 860°C (1472°F), and then returned to the reactor by a conveyor. The SO_x and CO₂ from catalyst regeneration are recycled to the gas exiting the reactor at 420°C (788°F), and the combined stream passes through the boiler air heater to recover the heat before being sent to desulfurization and/or the stack.

The chemical reactions for NO_x removal in the reactor with the CuO catalyst are given by Kurabo as follows:



In the presence of O₂,



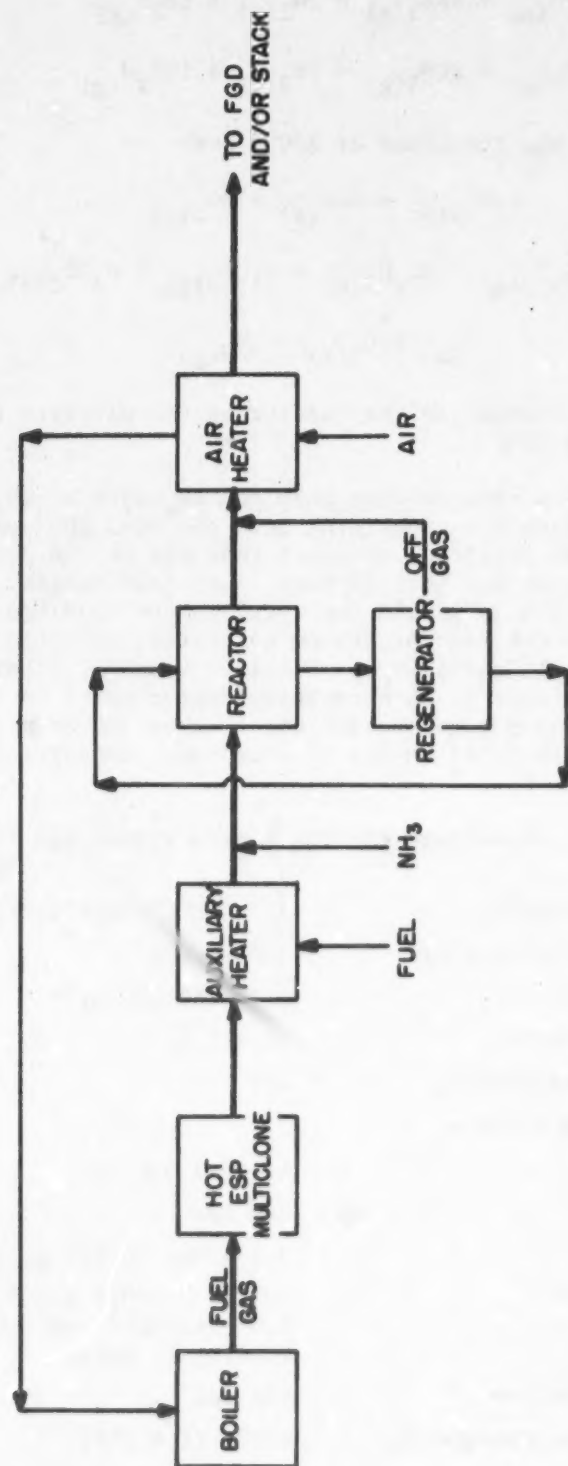
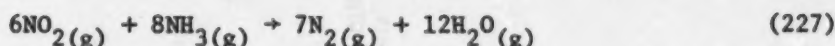
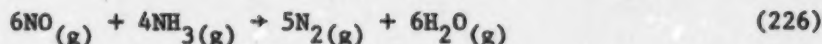
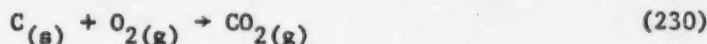
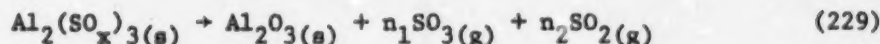


Figure 63. Flow Diagram of Kurabo Knorca Process.

Otherwise,



In regeneration, the reactions at 800°C are:



The $\text{Al}_2(\text{SO}_x)_3$ is created in the reactor as the catalyst (CuO) carrier, Al_2O_3 , reacts with the SO_3 .

The "Knorca" system removes more than 90% NO_x with an $\text{NH}_3:\text{NO}_x$ mol ratio of (0.9-1.2):1 and a flue gas containing 1600 ppm SO_2 , 280 ppm NO_x , and 0.1 g/ Nm^3 of dust (0.04 gr/sft³). Greater than 80% of the particulate loading is removed in the reactor but that is with inlet dust density of 0.1 g/ Nm^3 . Pilot-plant operation has indicated that particulate loadings of 1-2 g/ Nm^3 (0.43-0.86 gr/sft³) to the reactor may be tolerated, although collection efficiencies are not sufficient for particulate control. Therefore, an ESP is necessary to remove dust to an acceptable degree prior to the gas entering the reactor. The catalyst regeneration cycle takes 100 hr and the yearly loss by crushing is 5% of the total amount of catalyst. Catalyst life is estimated at 10,000 hr.

Typical operating conditions for the Knorca system are reported as follows:

Reactor temperature	350-400°C (662-752°F)
Pressure drop across bed	100 mm H ₂ O
Space velocity	7,000-10,000 hr ⁻¹
$\text{NH}_3:\text{NO}_x$ mol ratio	(0.9-1.0):1
NO_x removal efficiency	90%
Inlet gas composition	
SO_2	1,600-2,000 ppm
NO_x	300 ppm
Dust	0.1 g/ Nm^3 (0.043 gr/sft ³)
Dust removal	80% at 0.1-0.2 g/ Nm^3 (0.043-0.086 gr/sft ³) particulate loading at inlet
NH_3 at outlet	<10 ppm
Regeneration temperature	800°C (1,472°F)
Catalyst life	8,000-10,000 hr

Status of Development

Kurabo tested the Knorca system over a year on a 5,000 Nm³/hr flue gas capacity pilot plant with an oil-fired boiler. This pilot plant had a fixed catalyst bed in which pressure drop would increase after 30 hr of operation. To solve this problem, Kurabo made use of the moving catalyst bed. Problems were also experienced with NH₄HSO₄ deposits in the air heater. This was solved by reducing the NH₃:NO_x mol ratio to about (0.9-1.0):1. A 30,000 Nm³/hr capacity treatment plant was constructed by August 1975, and no problem has been observed during operation of this plant with pressure drop or NH₄HSO₄ formation.

The reactor handling 30,000 Nm³/hr of flue gas from an oil-fired boiler has three elements and each treats 10,000 Nm³/hr of flue gas. The average operating conditions are as follows:

NO _x inlet concentration	280 ppm
NO _x removal efficiency	93.6%
Particulate loading	94 mg/Nm ³ (0.04 gr/sft ³)
Gas volume	24,000 Nm ³ /hr
Space velocity	8,000 hr ⁻¹
SO ₂ inlet concentration	1,650 ppm
Gas temperature	400°C (752°F)
Pressure drop	65 mm H ₂ O
NH ₃ consumption	106.4 l/min
NH ₃ :NO _x mol ratio	1:1

Testing of effects of Cl⁻ on catalyst and aluminum (Al) support material and a new support material have been performed. As a result, a TiO₂ support system with an Fe-based catalyst has been selected for use where Cl⁻ concentrations exceed 100 ppm. The Al support had a tendency to irreversibly degrade at these Cl⁻ levels. The TiO₂ is inert to halogen poisoning and does not require extensive regeneration. Though more expensive, the TiO₂ is better when considering maintenance and operating costs for regeneration.

Background of Process Developer

Kurabo is a producer of chemical and textile products. The Kurabo Engineering Division was started in 1970 to develop pollution control systems. Kurabo has developed an FGD system which is in use at over 140 industrial sites. Other systems for wastewater treatment, H₂O purification, etc., have been created and are in wide spread use. TRW, Inc., a diversified worldwide organization, has exclusive rights for supplying Knorca systems for boilers in the U.S. and Canada. TRW has had over two decades of involvement with Japanese business and has been involved since 1971 with Japanese technology on pollution abatement. This process should be readily accessible to the U.S. market. Kurabo states that the Knorca system is now commercially available for oil-fired boilers.

Published Economic Data

The capital investment for a plant treating 500,000 Nm³/hr flue gas is about \$5.83M (68). This was for a boiler using C-class heavy oil, 8,400 hr/yr operating time, inlet gas NO_x concentration of 280 ppm and reaction temperature of 400°C (752°F). The revenue requirement equaled \$1.99M/yr (\$237.00/hr) or \$7.59/k1 of heavy oil (68). The capital investment is equivalent to about \$35/kW and revenue requirements are 1.4 mills/kWh. All these figures are assumed to be 1976 costs with Japan as site location.

Raw Material, Energy, and Operation Requirements

NH₃ is the only major raw material required for the Knorca system. With the NH₃:NO_x mol ratio of 1:1, the NH₃ usage for a 500,000 Nm³/hr gas capacity plant should be about 3.5 short tons/day at an NO_x inlet concentration of 300 ppm.

The fuel oil required is 749 k1/day for the same conditions as above in published economic data, which is equivalent to about 27.7 GBtu/day. The following electricity and steam requirements are also on the same basis as the above:

<u>Material</u>	<u>Quantity</u>
Electricity	1,169 kW
Steam	15.3 tons/day

The electrical requirement represents 0.7% of the total equivalent electrical output of the plant.

No details are available on operation and maintenance requirements, but the operation is simpler and should require less labor and maintenance than wet NO_x removal processes. The moving-bed and regeneration system probably require more maintenance than dry systems with a fixed bed and no regeneration. This system should not require any more technical support than any other dry NO_x removal process.

Technical Considerations

This system is simple and can be fully automated. The NH₃ flow rate control is based upon the inlet gas NO_x concentration and the gas volume. As a double check, the NH₃ usage rate is also compared with fuel consumption.

Experimental data from Kurabo show that O₂ has an effect on NO_x removal. As O₂ present in flue gas increases from 0-0.5%, the NO_x removal increases from about 50-90%. Above an O₂ level of 0.5%, the effect on NO_x removal remains constant.

The size of the reactor vessels should be similar to other dry NO_x removal processes with reaction temperatures in the range of 350-400°C (662-752°F) since the space velocity is about 7,000-10,000 hr⁻¹. An internal bucket conveyor is used for transferring the catalyst from the

regenerator to the top of the reactor of the 30,000 Nm³/hr size prototype unit. Since the catalyst flow rate is small, the particular conveyor used has a capacity over 100 times larger than necessary. Therefore, conveyors would be available that possess the capacity required for a 500-MW-size plant.

The regeneration unit for the 30,000 Nm³/hr capacity treatment facility has electrical heating. This method of heating would be too expensive for application to a large plant. The regeneration of the catalyst with hot air, rather than electrical heating, would be the preferred regeneration mode for large utility applications.

In retrofit application on a boiler with a cold ESP after the air heater, treatment of gas from the cold ESP would require reheat for the gas to reach reaction temperature. If a desulfurization unit is also present, treatment of gas from the FGD exit would require even more reheat. In the above cases, the hot ESP shown in the process flowsheet would be eliminated but a heat exchanger would be required for energy savings by allowing the hot treated gas to preheat the incoming, untreated gas. The operating costs for the above would naturally be greater since more reheat is required than for the case shown in the process flow diagram.

For treating flue gas from a 500-MW plant, several NO_x removal trains will be necessary. The turndown capability would primarily be the removal of a train from service. The auxiliary heaters provide reaction temperature control during boiler operating fluctuations.

The majority of the material of construction is carbon steel.

Environmental Considerations

There are no byproducts with the Kurabo process. Kurabo states that there were problems with NH₄HSO₄ formation early in development tests but that, since a lower NH₃:NO_x mol ratio and better control have been used, no problem with the formation has been encountered. Kurabo representatives state that if NH₄HSO₄ did form, that steam and H₂O would easily remove it; however, this procedure would require shutting down the NO_x removal unit and also a method for disposal of the washing solution. The NH₃ in the outlet is reported to be <10 ppm. The catalyst is not expensive enough to reclaim entirely, but the heavy metal portion is reclaimed.

Greater than 80% removal of particulate is reported by Kurabo. However, the inlet dust content was only about 0.1 g/Nm³ (0.043 gr/sft³) which is much smaller than particulate loading typical of a coal-fired boiler (about 15 g/Nm³; 6.4 gr/sft³). The maximum particulate loading to the reactor indicated from pilot tests is 1-2 g/Nm³ (0.43-0.86 gr/sft³). In some instances, it may be possible to use multiclones prior to the reactor in retrofit installation where secondary particulate control already exists downstream of this NO_x FGT system.

Critical Data Gaps and Poorly Understood Phenomena

The sensitivity of NO_x removal efficiency to such factors as temperature, space velocity, and SO_x inlet concentration are not yet reported.

Advantages and Disadvantages

The Kurabo Knorca process has the following advantages and disadvantages:

Advantages

1. Achieves >90% NO_x removal efficiency
2. Operates with moderate particulate loadings (up to 1 gr/sft³)
3. Claims <10 ppm by vol NH_3 in treated flue gas

Disadvantages

1. Has not been tested on coal-fired gas (has been tested on simulated coal-fired flue gas)
2. Uses moving-bed reactor which increases maintenance and catalyst attrition
3. May require auxiliary heater to attain or control reaction temperatures

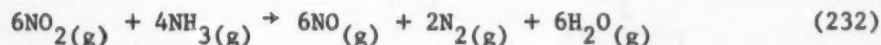
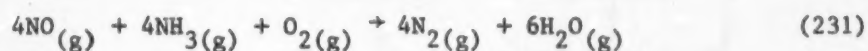
KUREHA PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (74, 75)

The Kureha process (Kureha Chemical Industry Company, Ltd.) is a dry NH₃-based SCR system and is specifically designed to be installed after an existing FGD system. Although not mentioned by Kureha, the catalyst is apparently sensitive to SO₂ and the pretreatment step has been added to remove most of the remaining SO₂ and dust. The process consists of three sections: pretreatment, heat exchange, and the reduction reactor. A block flow diagram is shown in Figure 64.

The flue gas from the boiler passes through a conventional FGD system before entering the denitrification system. The flue gas enters the pretreatment section of the Kureha system where any remaining SO₂ and dust are contacted with a very fine mist of alkali solution in a spray tower. The resulting SO₂ and dust-contaminated mist is then reportedly removed in a wet-type ESP.

The flue gas leaving the pretreatment section extracts waste heat from the clean exhaust gas exiting the NH₃ reduction reactor in a countercurrent heat exchanger and is heated to 130°C (266°F). NH₃ is injected and after the temperature of the flue gas-NH₃ mixture has been further increased to 150°C (300°F) by indirect contact with steam, it is sent to the catalytic reduction reactor where NH₃ selectively reduces NO_x according to the following reactions.



Since NO represents 90-95% of the NO_x in the flue gas, reaction (231) is the primary reaction occurring in the reduction reactor.

The gas from the reactor passes through the heat exchanger to heat the incoming flue gas before exiting through the stack.

Status of Development

The initial research and development work for the Kureha dry SCR process was begun in 1975 with the goal of developing a system which would be relatively inexpensive and could be installed after an existing wet FGD system. The resulting process was tested in a 300 Nm³/hr (0.1 MW equiv) bench-scale unit during 1976. The type and composition of the flue gas have not been disclosed. In late 1976 a 5000 Nm³/hr (1.6 MW equiv) pilot plant was built based on the results from the earlier bench-scale unit and the operation of this pilot plant was expected to begin in February 1977.

This process has not been tested on flue gas from a coal-fired boiler.

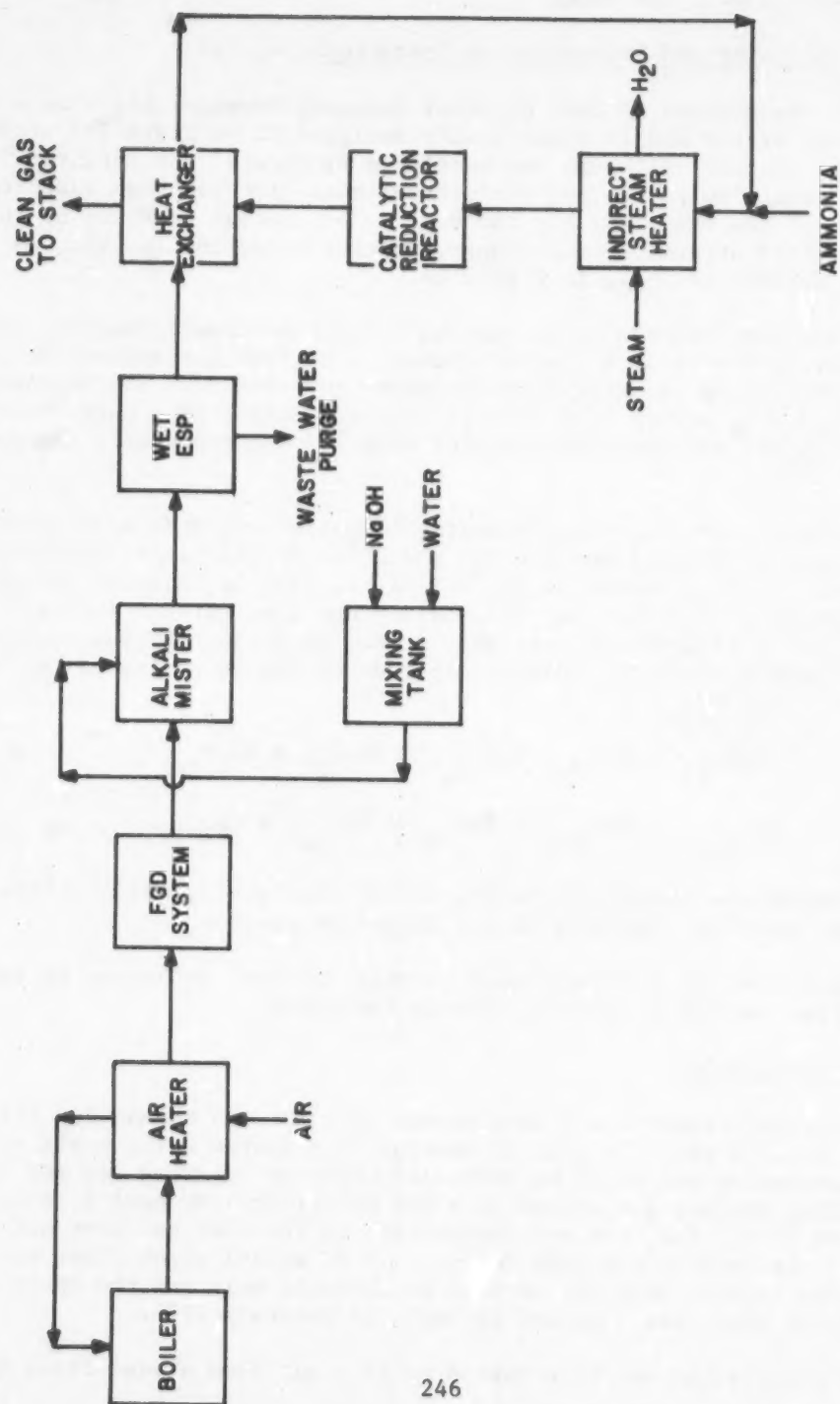


Figure 64. Flow Diagram of Kureha Process.

The next development step for this process would be the continuation of testing at their pilot plant to generate data for further scaleup to a prototype unit and also to demonstrate the long-term reliability of this system. The ability of this unit to treat flue gas from a coal-fired boiler also needs to be demonstrated.

Background of the Process Developer

Kureha is a medium-sized Japanese chemical company with major interests in fertilizers and petrochemicals as well as basic organic and inorganic chemicals. Kureha entered the air pollution control field in 1967 with the initial bench-scale testing of their Na_2SO_3 FGD system. After additional pilot-plant work during 1968, several commercial units based on this Na_2SO_3 FGD technology were completed during the early 1970's. This original Na process was modified in 1971 to incorporate acetic acid (CH_3COOH) in the scrubbing solution and this new system was renamed the sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$)- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ process. A bench-scale FGD unit using this $\text{NaC}_2\text{H}_3\text{O}_2$ - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ technology and treating $100 \text{ Nm}^3/\text{hr}$ (0.03 MW equiv) was built in 1973 and continued to operate until a pilot-plant treating $5000 \text{ Nm}^3/\text{hr}$ (1.6 MW equiv) of oil-fired flue gas was completed in March 1975.

Initial investigation into the possibility of modifying their $\text{NaC}_2\text{H}_3\text{O}_2$ - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ process to simultaneously remove SO_2 and NO_x was begun in late 1971. A bench-scale treating $250 \text{ Nm}^3/\text{hr}$ (0.08 MW equiv) of oil-fired flue gas was completed in 1973 and continued operation until mid-1974. The Kureha $\text{NaC}_2\text{H}_3\text{O}_2$ - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ process for simultaneous SO_2 - NO_x removal was scaled up to $5000 \text{ Nm}^3/\text{hr}$ (1.6 MW equiv) pilot plant in early 1976 and has been operating since then.

Kureha has recently begun the development of this NH_3 -based dry SCR process. The initial research for this SCR process was completed in 1975 and a bench-scale unit (0.1 MW equiv) was operated during 1976. In late 1976 a pilot plant (1.6 MW equiv) was constructed and testing was scheduled to begin in February 1977.

Kureha has offices in New York City which should make this process more accessible.

Published Economic Data

The estimated total capital investment and annual revenue requirement for the Kureha NH_3 -based SCR system are considered proprietary information by the process developer.

Raw Material, Energy, and Operation Requirements

The following raw material, energy, and operation requirements are preliminary estimates by Kureha and are based on a unit treating $100,000 \text{ Nm}^3/\text{hr}$ (33 MW equiv) of flue gas containing 50 ppm SO_2 , 200 ppm NO_x , and 0.1 g/Nm^3 of dust. The SO_2 and NO_x removal efficiencies were 99 and 90% respectively. Under these assumptions the raw material requirements would be as follows (all quantities in tons are assumed to be long tons).

<u>Raw material</u>	<u>Quantity</u>
NaOH	18 kg/hr
NH ₃	14 kg/hr
Catalyst	17.6 ton/yr

The utility requirements on the same basis are:

<u>Utility</u>	<u>Quantity</u>
Electricity	200 kW
Process water	1.0 ton/hr
Steam	1.65 ton/hr

By using the FGD system operators to also monitor the denitrification plant, no additional manpower will be required. The maintenance requirements have not been released.

Technical Considerations

The Kureha system is a relatively simple system consisting of the following three sections: a wet pretreatment section to remove particulates and some SO₂, a heat exchange section to preheat the incoming flue gas, and the reduction reactor. The only major process control problem will be the injection of the exact amount of NH₃ required to provide an NH₃:NO_x mol ratio of (1.0-1.1):1 in the catalytic reduction reactor. This NH₃ feed rate is automatically controlled by measuring the inlet flue gas rate and injecting a proportionate amount of NH₃.

The NO_x removal efficiency is relatively independent of the inlet flue gas composition providing that the particulates and SO₂ levels are kept below 0.2 g/Nm³ and approximately 50 ppm respectively. These incoming particulate and SO₂ levels are reported to be further decreased to 1 mg/Nm³ of dust and 1 ppm SO₂ in the Kureha pretreatment section. At high dust levels the catalyst pellets will become covered and the number of active sites available for NO_x reduction will decrease. In addition, this dust coating will also plug some of the reactor internals and significantly increase the pressure drop through the reactor. Failure to remove most of the SO₂ in a conventional FGD system prior to entering the pretreatment section of the Kureha process will result in the formation and precipitation of corrosive NH₄HSO₄ on the reactor internals and hence sharply decrease the NO_x removal efficiency.

The catalytic reduction reactor is a fixed-bed type. The catalyst particles themselves are somewhat unusual in that they are made entirely from the active base metal without any carrier such as Al₂O₃ or activated C. The nature of the base-metal catalyst is proprietary but the catalyst particles are shaped into pellets with typical dimensions of 5 mm in dia and 10 mm in length. For 90% NO_x removal the operating conditions in the reactor are:

Parameter	Value
NH ₃ :NO _x mol ratio	(1.0-1.1):1
Temperature	150°C (302°F)
Space velocity	5,000 hr ⁻¹
Superficial velocity	0.75 m/sec
Catalyst size/shape	5 mm dia x 10 mm pellet

These operating parameters in the reduction reactor are very similar to those specified by the other NH₃-based dry SCR processes except for the operating temperature. Since the Kureha system is added after a conventional FGD system and the flue gas is further treated to reduce the inlet SO₂ concentration to about 1 ppm, the formation and precipitation of NH₄HSO₄ should not be a significant problem under normal operating conditions.

Unlike most of the other dry, NH₃-based, SCR processes, a failure of the conventional FGD unit will also require shutting down the NO_x removal system. By using a higher reaction temperature the other processes eliminate the problem of NH₄HSO₄ formation and are not dependent on the FGD system performance.

Since this process is added after the FGD system, the Kureha system should be relatively easy to retrofit to an existing power plant providing sufficient land area is available nearby for siting the process equipment.

Although not mentioned by the process developers, it has been assumed that two trains of denitrification equipment will be required for a 500-MW coal-fired boiler. With each of these trains rated at approximately 55% of the total capacity, this system should be able to cycle with the boiler.

With the exception of the pretreatment section, apparently only mild carbon steel will be required for the remaining equipment. The equipment and piping in the prescrubbing section will probably be constructed from elastomer-lined carbon steel.

Environmental Considerations

The Kureha dry process has been able to average 90% NO_x removal during bench-scale testing. To maintain this high NO_x removal efficiency the particulate and SO₂ levels in the incoming flue gas must be kept to a minimum. In addition, failure to maintain an NH₃:NO_x mol ratio of at least 1:1 in the reduction reactor will result in a decline in the NO_x removal efficiency.

This process, although designed for NO_x removal, also removes residual SO₂ and particulates.

Critical Data Gaps and Poorly Understood Phenomena

Because of the relatively new development status of the process, critical data gaps or poorly understood phenomena are not given.

Advantages and Disadvantages

Advantages and disadvantages of the dry Kureha process are listed below.

Advantages

1. Achieves >90% NO_x removal efficiency
2. Operates between 100 and 200°C, which may require only negligible reheat

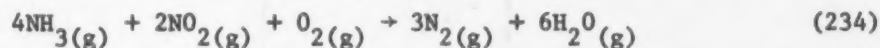
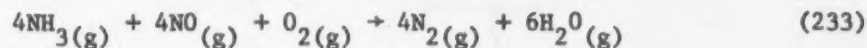
Disadvantages

1. Forms secondary source of pollution (Na₂SO₃-ash sludge waste stream)
2. Has not been tested on coal-fired flue gas
3. Requires clean (SO₂- and particulate-free) gas feed

MITSUBISHI HEAVY INDUSTRIES PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (5, 20, 41)

Mitsubishi Heavy Industries, Ltd., (MHI) has developed a dry, SCR method for NO_x removal using NH₃ as the reduction agent. A block flow diagram of the MHI process for treating a coal-fired flue gas is shown in Figure 65 and is based on the arrangement used in the pilot-plant treatment of dirty flue gas. The flue gas exiting the boiler-economizer has the majority of particulate matter removed by passage through a hot ESP. The flue gas exiting the ESP is heated to reaction temperature by an auxiliary heater. The flue gas having been injected with NH₃ enters the reactor where, at the required temperature and in the presence of the catalyst used by MHI, the NO_x is converted to N₂ by reaction with NH₃ as follows:



The treated flue gas leaves the reactor and passes through an air heater to transfer the heat from the treated flue gas to the air feeding the boiler. The flue gas passes from the air heater to a desulfurization unit and/or the stack.

The reaction temperature ranges from 350-400°C (662-752°F), the average NH₃:NO_x mol ratio employed is 1:1 and the NO_x removal efficiency averages above 90%. The pressure drop and space velocity will vary based upon whether a fixed- or moving-bed or parallel passage reactor is used. The space velocity for the fixed- and moving-bed reactor varies from 4,000-10,000 hr⁻¹ on semidirty gas while the range tested for parallel passage reactors is 1,000-2,300 hr⁻¹ for dirty gas. MHI created a special "W"-shaped vessel enabling the catalyst to be intermittently moved downward through the reactor. (Refer to critique topic Technical Considerations.) MHI is also testing a parallel passage reactor.

Status of Development

MHI has tested the SCR methods at pilot plants on both clean and dirty flue gas. A 10,000 Nm³/hr (3.3 MW equiv) capacity pilot plant treating flue gas from an LNG-fired boiler at Minamiyokohama Station of Tokyo Electric was used for clean gas treatment studies. Several base-metal catalysts on Al₂O₃ carriers and combinations thereof were tested for NO_x reduction capability and the amount of NH₃ emitted in the outlet gas. The catalyst providing the best results were composed of chromic oxide (Cr₂O₃) with other oxides, e.g., Fe₂O₃-Cr₂O₃ and vanadium pentoxide-chromic oxide (V₂O₅-Cr₂O₃). A catalyst life test indicated no reduction in activity after 5500 hr service.

Experiments on the dirty gas were performed on a 4000 Nm³/hr (1.3 MW equiv) capacity pilot plant on gas from a low-S oil. The gas contained 160 ppm NO_x, 80 ppm SO₂, 3 ppm SO₃, and 20 mg/Nm³ (0.009 gr/sft³) of particulates.

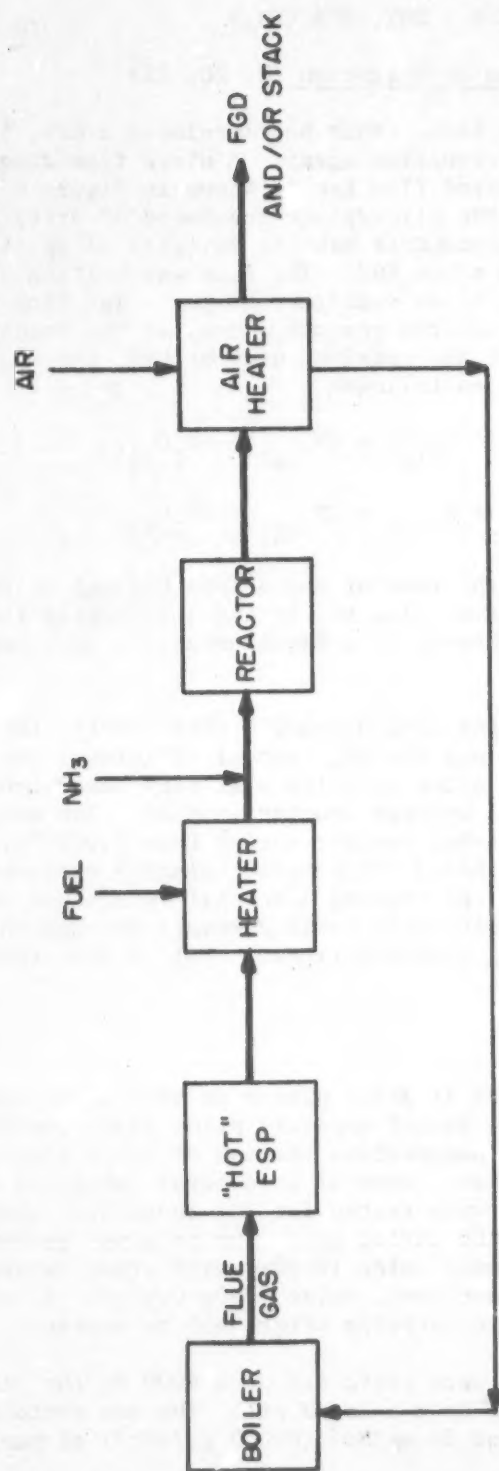


Figure 65. Flow Diagram of Mitsubishi Heavy Industries Process.

The metal catalysts evaluated include nickel (Ni), Co, Fe, manganese (Mn), chromium (Cr), V, and Co and combinations thereof. The most SO_x -resistant catalyst carriers were TiO_2 and SiO_2 . There were two units in the pilot plant. One incorporated a fixed-bed reactor and the other unit contained an intermittently moving-bed reactor. There was no loss in catalyst activity after a 1500-hr test with the fixed-bed reactor. A list of some of the pilot plants operated or planned for operation by MHI is given in Table 28. It should be noted that both moving-bed reactors and parallel passage reactors are being investigated. The NO_x removal facilities for treating clean or semidirty gas are considered commercially available. Tests have been conducted on coal-fired boilers for at least 660 hr with the use of a hot ESP. Future tests are planned for sending the flue gas containing 15 g/Nm^3 of particulate directly to the parallel passage reactor.

Background of Process Developer

MHI has been developing a SCR process since 1973 in laboratory and pilot-plant tests. Two NO_x removal facilities are scheduled to be constructed by MHI for Kyushu Electric in 1978-1979 on two 600-MW LNG-fired boilers. Other FGT units constructed by MHI include removal facilities for 382,000 (127 MW equiv) and 200,000 Nm^3/hr (67 MW equiv) heavy oil-fired boilers. These were scheduled to start operation in September 1976 and December 1977 respectively.

Published Economic Data

No economic data have been published.

Raw Material, Energy, and Operation Requirements

There is no information stated by MHI on raw material and energy requirements. However, it may be estimated that 20 short tons/day of NH_3 , the major raw material required, is necessary to treat flue gas from a 500-MW plant containing 600 ppm NO_x if an $\text{NH}_3:\text{NO}_x$ mol ratio of 1:1 is used. The major energy sources required are fuel for the heater and electricity. No manpower, maintenance, and technical support requirements are available.

Technical Considerations

The MHI process includes straightforward and simple steps and is much less involved than wet NO_x removal systems. The NH_3 injection rate would probably be controlled by the flue gas rate and NO_x concentration. The fuel rate to the auxiliary heater would be controlled by the reactor temperature.

During the pilot-plant work on clean gas, the effect on NO_x removal of flue gas O_2 content was studied and the results are shown in Figure 66. (The particular catalyst used is not known.) As can be seen, with a space velocity of $10,000 \text{ hr}^{-1}$ and an $\text{NH}_3:\text{NO}_x$ mol ratio of 1:1, the NO_x removal efficiency with 0% O_2 in the flue gas was very low as compared to NO_x removal efficiency with levels of 0.5% O_2 and greater. For example, at 375°C , the denitrification achieved was about 90% at a 1% O_2 level while only about 50% NO_x removal was achieved at an O_2 level of 0%.

TABLE 28. ACTUAL OR DESIGNED OPERATING CONDITIONS^aOF NO_x REMOVAL PILOT PLANTS (41)

BY MITSUBISHI HEAVY INDUSTRIES

Flue gas source	Capacity, Nm ³ /hr	Inlet flue gas composition SO ₂ , ppm	Particulates, mg/Nm ³	Space velocity, hr ⁻¹	Reactor type	Exit NH ₃ concentration, ppm by vol	NO _x minimum removal efficiency, %	Operating period, hr
LAG	1,000	0	0	10,000-20,000	Fixed	10	90 at 10,000 hr ⁻¹ S.V.	10,000
Low S oil	5,000	200	20-130	5,000-10,000	Fixed and moving	20	90 at 5,000 hr ⁻¹ S.V.	5,000
Low S oil	60	200	20-130	6,000	Fixed	10	90 at 6,000 hr ⁻¹ S.V.	2,600
High S oil	1,000	900	70	10,000	-	10	90	-
High S oil	500	600	60	7,000	-	7	95	6,000
-	10,000	100	10	10,000	Fixed and moving	5	95	4,000
High S oil	10,000	1,050	50-100	8,000-10,000	Fixed and moving	5	95	2,500
Low S oil	10	100	10-20	10,000	Fixed	8	95	6,200
Sintering mill	500	400	-	8,000-10,000	-	5	96	3,000
Heavy S oil	240	800	100-150	2,300	Parallel passage	-	-	Design
Heavy S oil	500	600	60	-	Parallel passage	-	-	Design
Heavy S oil	2,000	800-1,000	30-70	-	Parallel passage	15	85	Design
Low S oil	40,000	150	15-30	1,000	Parallel passage	10	90	Design
Coal	600	1,000-1,900	15,000 ^b	1,000	Parallel passage	-	90	Design ^b

a. The data reported for the latter five units are design conditions; other data are from actual test operations.

b. Tests have been completed for 660 hr operation during which the particulate concentration was 15 g/Nm³. The design conditions assumed to have been met.

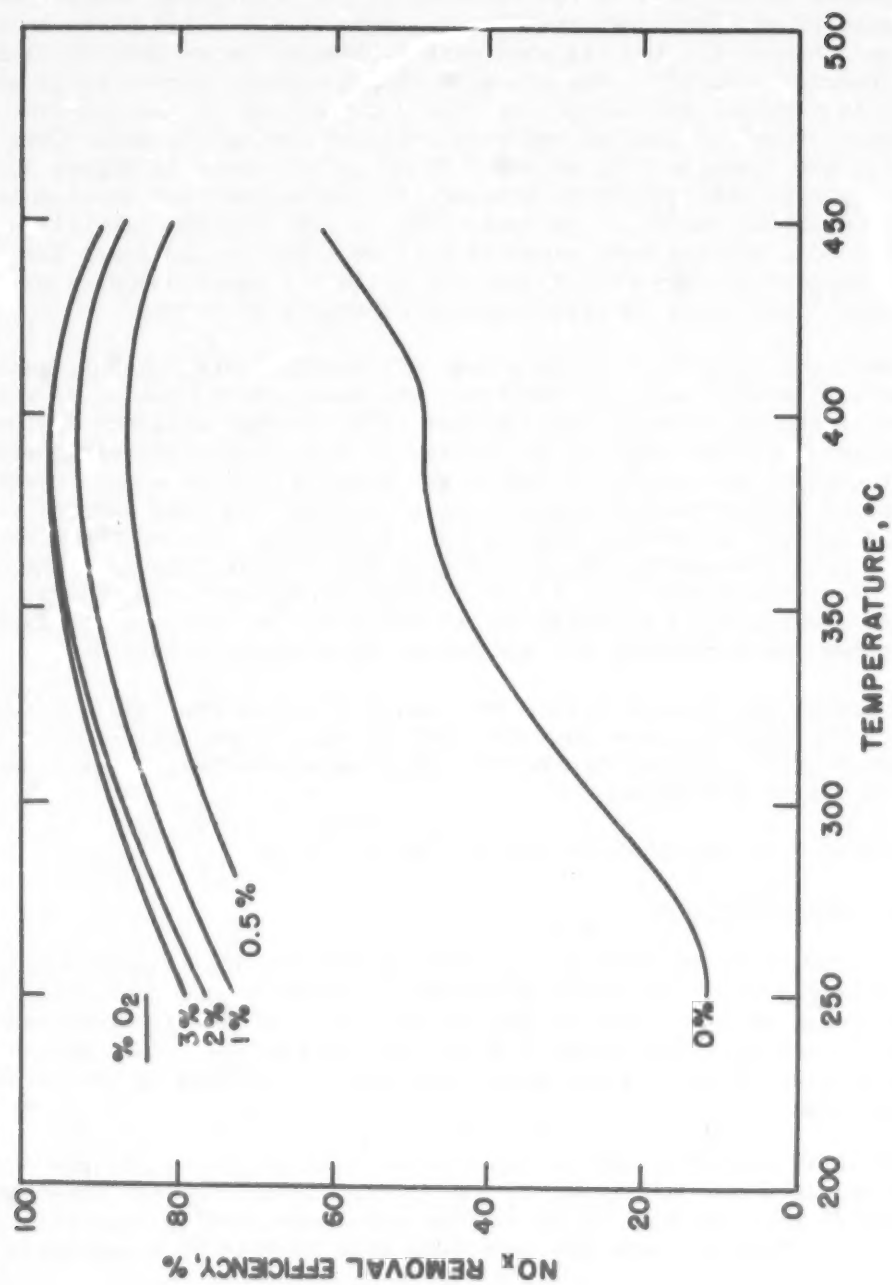


Figure 66. Results from MHI's Pilot-Plant Tests Showing Effect of Oxygen on NO_x Removal Efficiency (20).

In early bench-scale experiments on fixed beds with the dirty flue gas, plugging problems were experienced on catalyst 3 mm in diameter. Catalyst of 8-mm diameter reduced the problem of plugging but the NO_x removal efficiency decreased. Therefore, later work used a catalyst of 4-6 mm in diameter.

The W-shaped vessel used in the interior of the moving-bed reactor as shown in Figure 67 was developed by MHI. In tests at the pilot plant on the dirty flue gas, the moving bed was used with a catalyst layer 100-200 mm deep and in the absence of an ESP. The pressure drop increased from 7 to 13 mm $\text{H}_2\text{O}/\text{day}$ till it attained 160 mm H_2O ; at this point 10-20% of the catalyst would be removed from the reactor and supplanted by moving the bed. This action lowered the pressure drop to about 60 mm H_2O as shown in Figure 68. The catalyst exiting the reactor is screened to remove dust and is circulated back to the top of the reactor. In comparison to most dry NO_x removal processes, the size of equipment required will probably be similar. The reaction temperature of 350-400°C is typical while the space velocity of 4,000-10,000 hr^{-1} is in the average range of other dry processes.

If retrofitted to a plant after a cold ESP located after the air heater, a large amount of reheat would be required. An even greater amount of reheat is necessary if the NO_x removal facility has to be located after an FGD unit. A heat exchanger would be required for energy savings by transferring heat from the hot treated gas to the untreated gas going to the reactor. Operating costs for any of these retrofit cases would be greater than the process shown in the flow diagram. If tests prove that it is feasible to send the flue gas directly to a parallel-passage reactor without particulate removal, this scheme will provide a significant saving in capital and operating costs. However, this process would probably not be suitable for retrofit and lack of space between the economizer and air heater in existing plants.

Since several NO_x removal trains are needed for treating flue gas from a 500-MW plant, the main turndown control would be removal of individual trains. The auxiliary heater would provide better reaction temperature control during variations in boiler operations.

The materials of construction are not given.

Environmental Considerations

The sensitivity of NO_x removal to reaction temperature and space velocity is indicated in Figure 69 for tests performed on fixed-bed reactor with dirty flue gas and using an ESP. With an $\text{NH}_3:\text{NO}_x$ mol ratio of 1:1, a space velocity of 10,000 hr^{-1} , and at 360°C, about 90% NO_x removal was achieved. Figure 70 shows sensitivities of NO_x removal efficiency and NH_3 exiting in the outlet gas to boiler load.

The amount of NH_3 which may be expected to exit in the outlet gas should average <10 ppm as shown in Figures 70 and 71 from tests on clean flue gas and in Figure 72 from the work on dirty flue gas. The results from pilot-plant tests with clean gas when NH_3 emissions were lowered by a catalytic

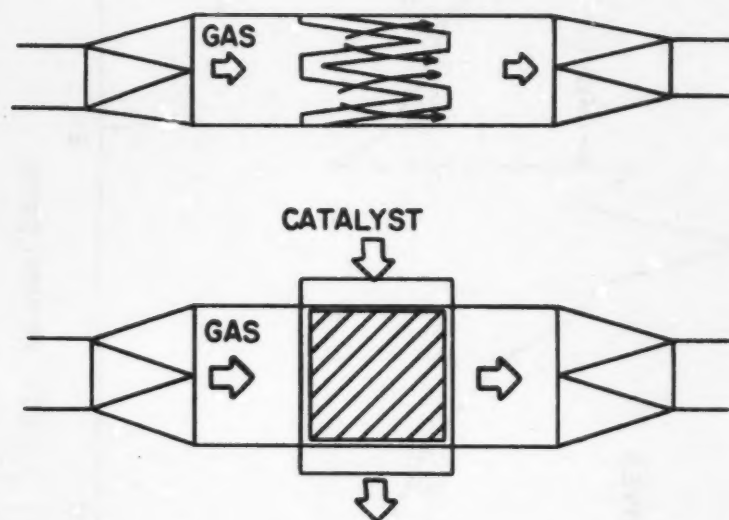
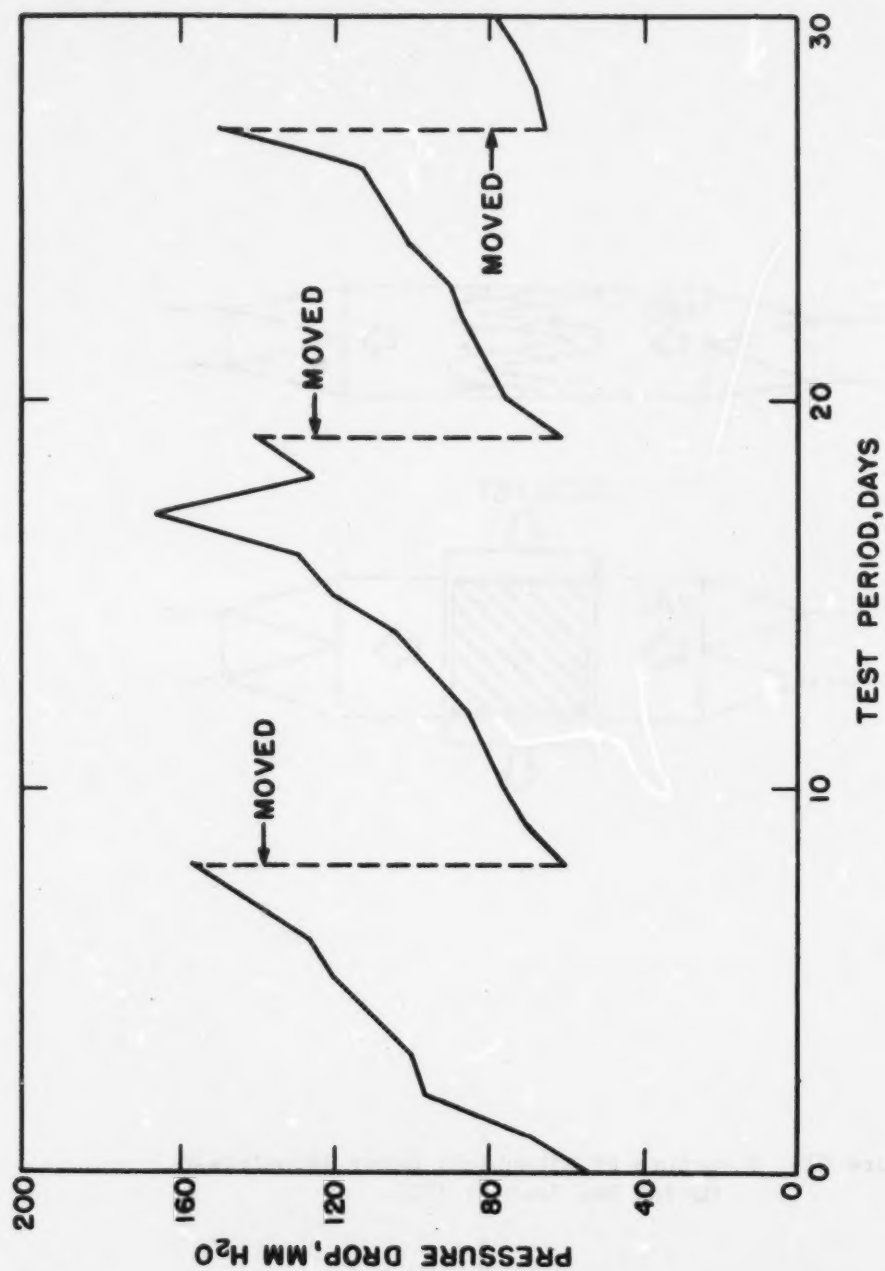


Figure 67. Structure of Mitsubishi Heavy Industries' Moving-Bed Reactor (20).



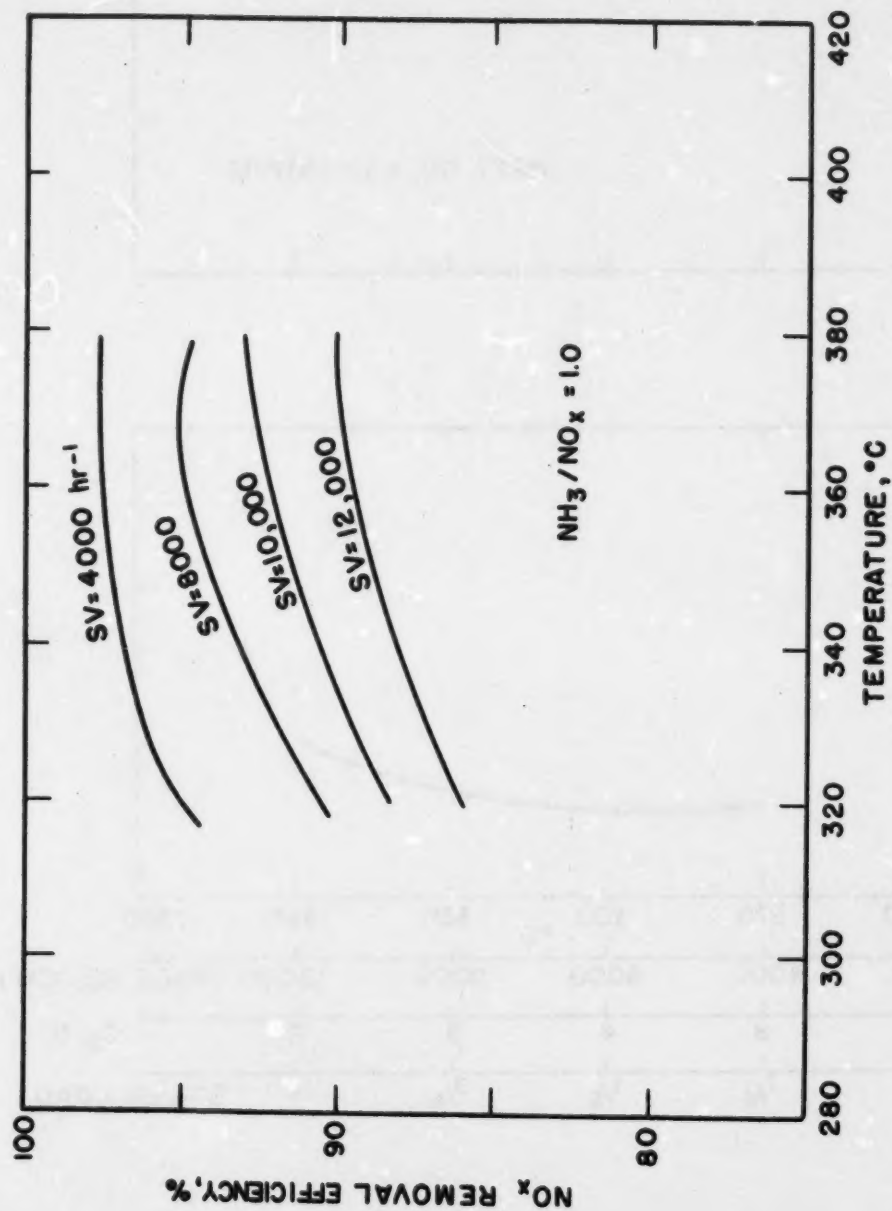


Figure 69. Results of Tests with Fixed-Bed Reactor and Dirty Flue Gas After Use of an ESP Showing Effects of Temperature and Space Velocity on NO_x Removal Efficiency for MHI Process (20).

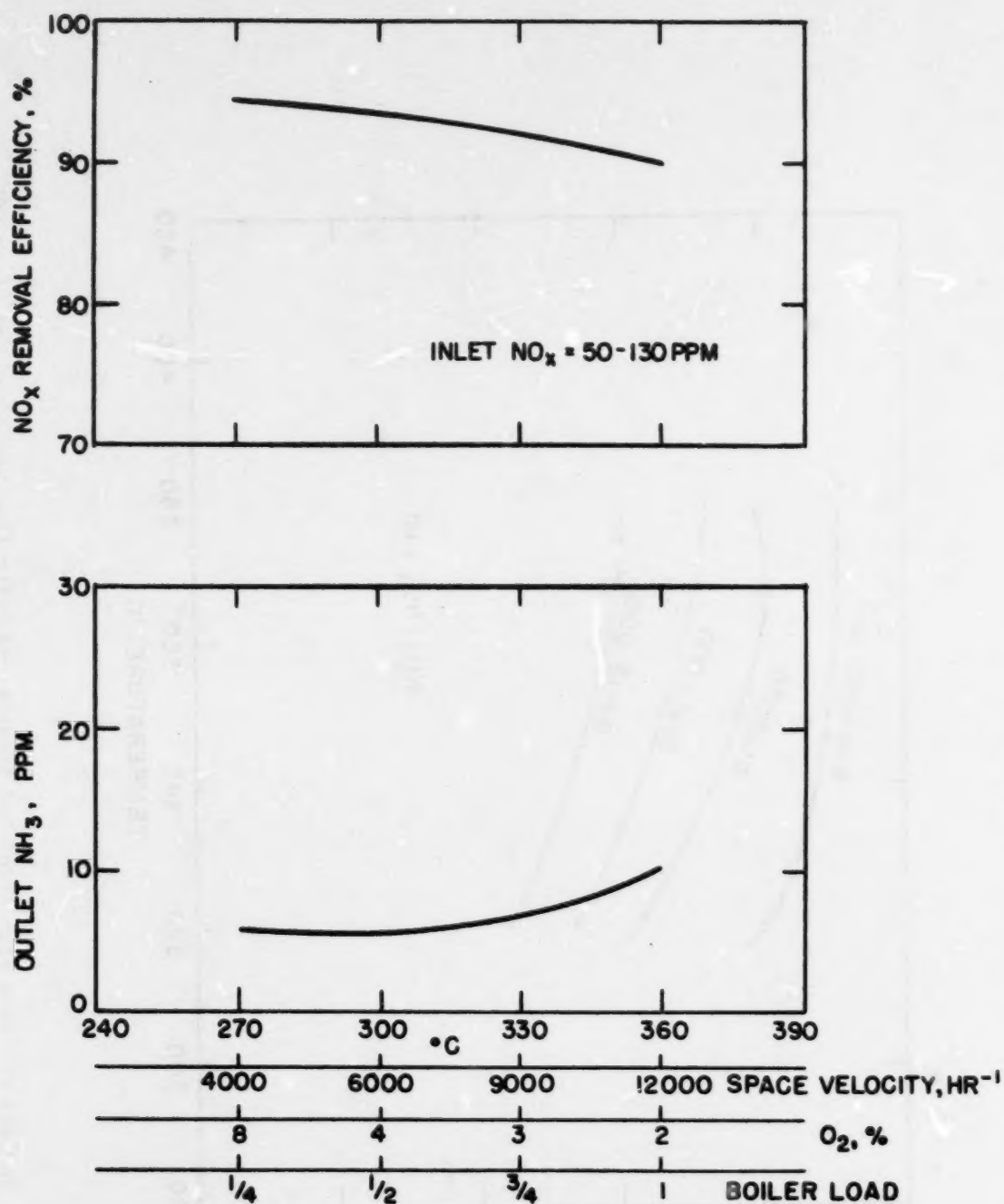


Figure 70. NO_x Removal Efficiency and Outlet Gas NH₃ Concentration at Different Boiler Loads for MHI Process (20).

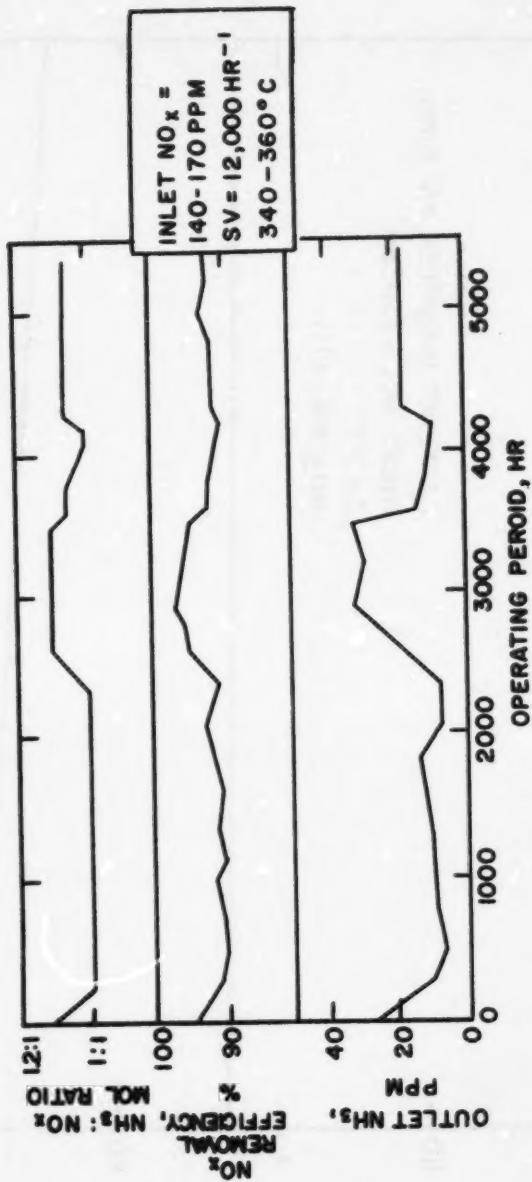


Figure 71. NO_x Removal Efficiency and NH₃ Emission in Relation to NH₃:NO_x Mol Ratio and Operating Period for MHI Process (20).

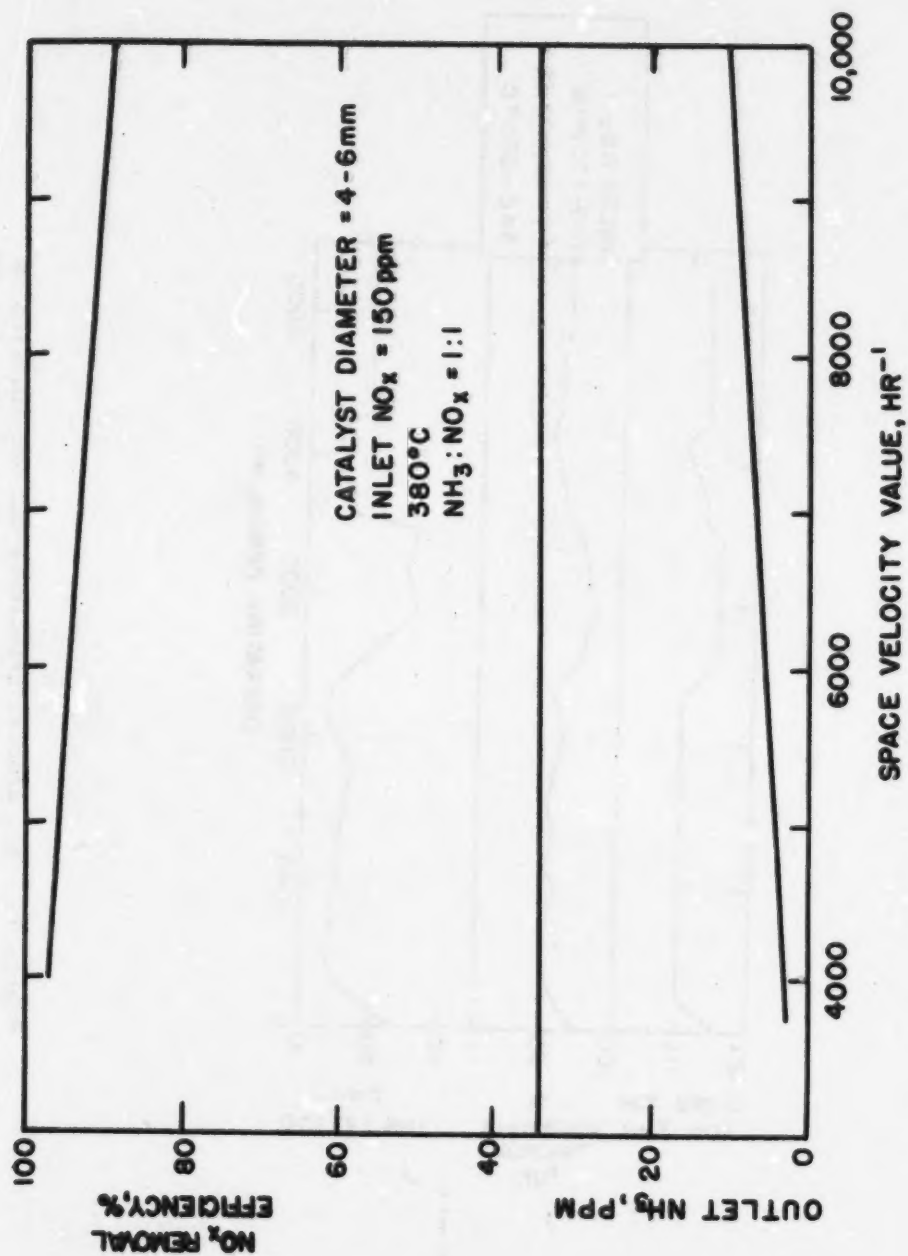


Figure 72. Effect of Space Velocity on NO_x Removal Efficiency and NH₃ Emission for MHI Process (20).

decomposer located after the reactor are shown in Figure 73. A denitrification efficiency of 97% was obtained while the NH_3 was decreased to 1-2 ppm in the outlet flue gas.

During pilot-plant tests with dirty flue gas, the deposits of NH_4HSO_4 on the air heater were measured and the results are shown in Figure 74. At 200°C (392°F), the maximum deposit was experienced. Steam blowing or washing with water could remove the buildup.

No information is available on the possible interference by other gas species. There are no apparent unusual work hazards.

Critical Data Gaps and Poorly Understood Phenomena

Though several of the catalysts tested are given, the specific catalyst selected by MHI for process use is not known. Also unspecified are the economics such as capital investment and revenue requirements. The raw material and energy requirements are not stated by MHI. The manpower, maintenance, and technical requirements, in addition to the materials of construction are also unknown. The maximum tolerable particulate loading is not known.

Advantages and Disadvantages

The advantages and disadvantages of the MHI process are as follows:

Advantages

1. Achieves >90% NO_x removal efficiency
2. Has been applied to flue gas from commercial oil-fired boilers
3. Claims <10 ppm by vol NH_3 in treated flue gas

Disadvantages

1. Requires somewhat clean (indefinite level of particulate removal required) gas feed
2. Uses moving-bed reactor which increases maintenance and catalyst attrition
3. Requires auxiliary heater to attain or control reaction temperatures

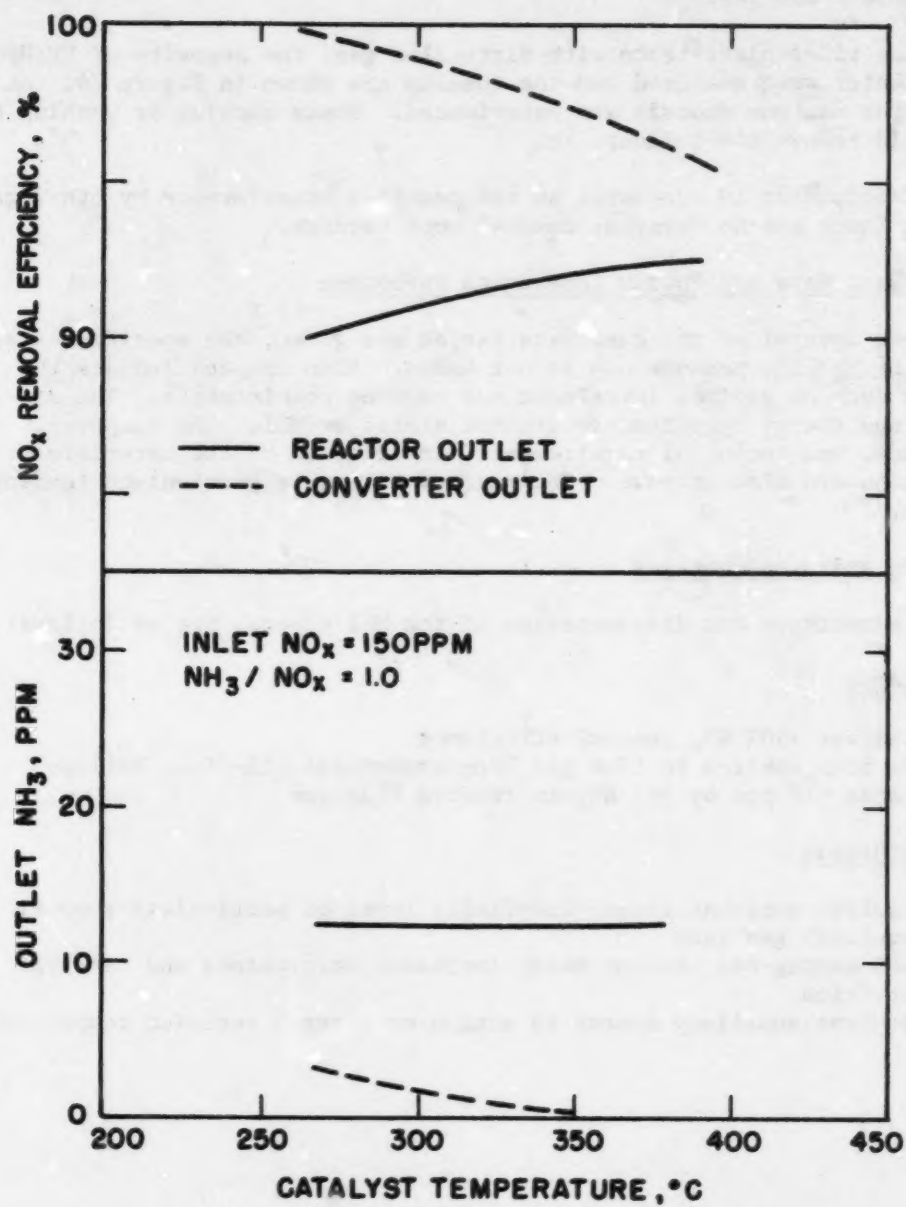


Figure 73. Results of MHI's Tests on NO_x Removal Efficiency and NH₃ Emission Using an NH₃ Converter to Reduce NH₃ Emission (20).

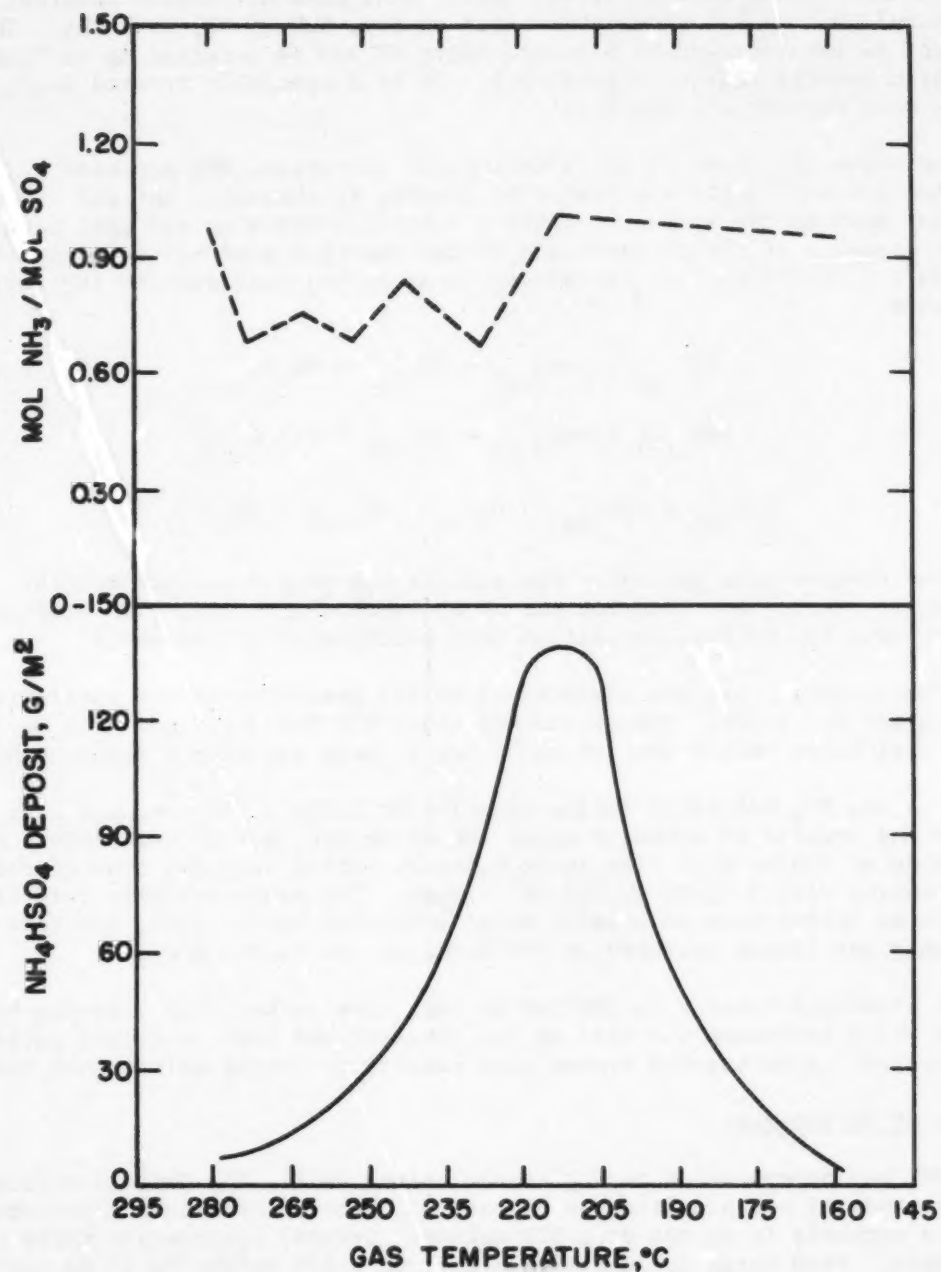


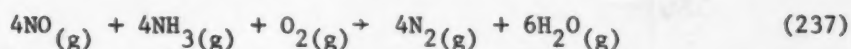
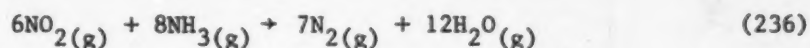
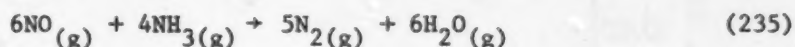
Figure 74. Deposit of $\text{NH}_3\text{-SO}_4$ Compounds in Air Reheater from MHI Tests (20).

MITSUBISHI KAKOKI KAISHA PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (41)

The Mitsubishi Kakoki Kaisha, Ltd., (MKK, also Mitsubishi Chemical Machinery) NO_x removal process is based on dry, SCR of NO_x with NH₃. The catalyst is manufactured by Santetsu Kogyo KK and is referred to as "SARC" (Santetsu Ammonia Reduction Catalyst). It is a specially treated Fe₂O₃·H₂O and is made without any carrier.

As shown in Figure 75 for a coal-fired operation, MKK proposes to treat the flue gas before the air heater by passing it through a hot ESP, injecting NH₃, and passing the mixture through a reactor containing the SARC catalyst. In the presence of the catalyst and at the reaction temperature range of 400-450°C (752-842°F), NO_x is reduced to N₂ by NH₃ according to the following reactions.



The treated flue gas exits the reactor and passes through the air heater for heating the incoming air which feeds the boiler. The treated gas is then sent to the desulfurization unit and finally to the stack.

The required reaction temperature varies according to the particulate loading and SO₃ level. MKK recommends 400-450°C for dirty gas with SO₃ as for a coal-fired boiler and 250-300°C for a clean gas with a trace of SO₃.

The NH₃:NO_x mol ratio varies from 1:1 to 1.3:1. The pressure drop across the reactor is normally about 80-160 mm H₂O, but it can reach a maximum value of 400 mm H₂O. The space velocity varies as a function of the dust content with a 3,000-10,000 hr⁻¹ range. The space velocity for the coal-fired boiler case is usually about 3000-5000 hr⁻¹. Also, the most favorable gas linear velocity in the catalyst bed is 3-5 m/sec.

A fixed-bed reactor is applied in this case rather than a moving-bed system which increases the wear on the catalyst and thus increases catalyst consumption. A moving-bed system also results in larger maintenance cost.

Status of Development

MKK has been working on NO_x removal since 1972. The initial effort was in the study of wet simultaneous SO_x and NO_x removal processes. However, now the emphasis is on the dry, SCR method. Several bench-scale tests have been made. From March to July 1975 a test on a 800 Nm³/hr (0.27 MW equiv) capacity bench-scale unit was made using flue gas from a coke oven. A test

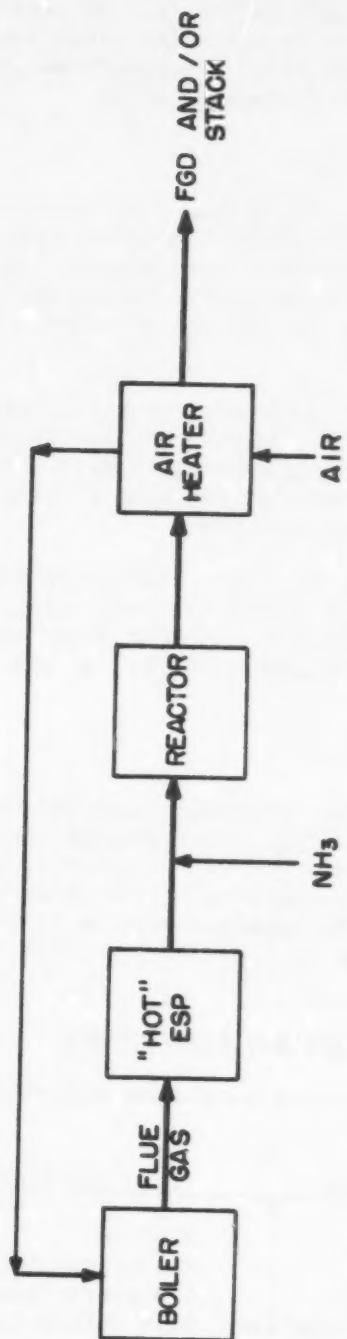


Figure 75. Flow Diagram of Mitsubishi Kakoki Kaisha (MKK) Process.

employing furnace flue gas at a rate of 100 Nm³/hr (0.03 MW equiv) began in June 1975, while in July another run began on a low-S, heavy oil flue gas source with a gas capacity of 1400 Nm³/hr (0.47 MW equiv). The latter two test units were still in operation as of April 1976. Also as of the same date, a pilot plant treating 1500 Nm³/hr (0.5 MW equiv) of gas from a high-S heavy oil-fired boiler had been in operation since September 1975. A 2000 Nm³/hr (0.67 MW equiv) capacity plant treating flue gas of a steel-ore sintering machine began operation in January 1976.

Background of Process Developer

MKK has supplied at least 13 Wellman-Lord desulfurization units with capacities of 30,000-1,200,000 Nm³/hr (10-400 MW equiv) since June 1971. Four lime-CaSO₄·2H₂O FGD plants have been constructed since March 1973 with 35,000 to 250,000 Nm³/hr (12-83 MW equiv) FGT capacity. Two other FGD plants treating 70,000 to 370,000 Nm³/hr (23-123 MW equiv) flue gas have been built since June 1973.

There are two pilot-plant size NO_x removal plants constructed by MKK which were to start up in 1976. One has a capacity of 5000 Nm³/hr (1.7 MW equiv) with clean flue gas from a heating furnace. The other plant treats 14,000 Nm³/hr (4.7 MW equiv) of flue gas from a boiler fired with high-S fuel oil at Nihon Yakin, Kawasaki Works.

The licensing rights for the SARC catalyst in the U.S. are held by Pfizer, Inc. This arrangement should make the accessibility of the MKK process more convenient to the U.S. The catalyst supply capacity of Santetsu is 300 tons/mo and MKK claims it holds top priority in having catalyst orders supplied.

Published Economic Data

The capital investment for a 400-MW plant is reported to be \$14.33M which is equivalent to \$36/kW (41). The revenue requirement is 1.8 mills/kWh or \$5.1 M/yr (41). These costs are on the basis of 150 ppm NO_x, 7000 hr/yr, space velocity = 5000 hr⁻¹, catalyst entirely replaced every 2 yr, and four equal NO_x removal trains. The catalyst cost is listed as about \$8,000/metric ton. These figures are based on \$1 = 300 yen, 1976 costs, and a Japanese location.

Raw Material, Energy, and Operation Requirements

For the 400-MW basis, as above, the raw material and energy requirements are as follows:

Material	Quantity
Electricity	2360 kW
Steam	2.9 metric tons/day
NH ₃	4.0 metric tons/day
Catalyst consumption	0.18 metric tons/day

The electrical usage represents 0.6% of the total equivalent plant power output. The estimated labor required for this plant is 12 man-hour/day. No maintenance or technical support requirements are available but they should be similar to other fixed-bed, dry NO_x removal systems and less than that required by wet processes.

Technical Considerations

This system is rather simple and automatic control of the NH₃ flow rate is possible, though not mentioned by MKK. The size of the required reactor should be slightly larger than some of the different processes since it has a space velocity of 3000-5000 hr⁻¹ and reaction temperature of 400-450°C (752-842°F).

For retrofit application on a system with a cold ESP and FGD unit it would be necessary to use an inline heater to heat the gas to the 400°C reaction temperature and a heat exchanger to recover the heat from the treated gas for the incoming, untreated gas. Less reheat would be needed if the gas could be treated prior to the FGD unit. Even for application on a new coal-fired plant, an inline heater may be required between the hot ESP and reactor since the gas from the boiler-economizer is most often considered to be only 375°C (705°F).

The SARC catalyst is Fe₂O₃ recovered from a steel pickling waste liquor. The catalyst can be made into any shape but presently is produced in five standard sizes. SARC I-IV are all ring shaped and are progressively smaller in size while SARC-P is a cylinder-shaped pellet. This cylinder-shaped catalyst is recommended for flue gas with high particulate loading and where stacking of catalyst would be required.

The turndown capability of this system is mainly by removal of an NO_x removal train from service. There would be several trains required for treating gas from a 500-MW-size plant.

The materials of construction are not given by MKK.

Environmental Considerations

MKK claims that there is no problem with the excess NH₃ exiting the system with a reaction temperature of 400°C (752°F) or greater while the excess NH₃ will exit at temperatures below 250°C (482°F). No mention of NH₄HSO₃ formation is made. There is no removal of pollutants other than NO_x.

For a pilot plant with oil-fired boilers, >90% NO_x removal was attained with NH₃:NO_x mol ratio of 1.2:1, reaction temperatures >300°C (572°F), space velocity of 5000 hr⁻¹, and inlet gas concentration of 200 ppm NO_x and 400 ppm SO_x. An 80% NO_x removal efficiency can still be reached with higher space velocities, such as 5,000-10,000 hr⁻¹. Tests underway on a steel-ore sintering plant have demonstrated that high level of Cl⁻ (exact level not specified) do not adversely affect the SARC catalyst.

At the 14,000 Nm³/hr pilot plant at Nihon Yakin, the operating conditions employed are as follows:

Reactor temperature	350°C
NH ₃ :NO _x mol ratio	1.2:1
Space velocity	3,000 hr ⁻¹
Linear velocity	6.8-7.3 m/sec
Inlet gas SO _x content	800-1,000 ppm
Inlet gas NO _x content	100-150 ppm

The NO_x removal which was achieved was about 95%. The catalyst arrangement was then changed from a staggered to a stacked packing arrangement (decreasing effective catalyst surface by 19%) to reduce accumulation of particulate matter in the catalyst bed. The NO_x removal subsequently declined from 95 to 85%. The man-hours required for stacking the catalyst on this 4.7-MW equiv-plant were 160.

The waste catalyst is a potential raw material for pigment production which may eliminate problems with disposing of the catalyst.

Critical Data Gaps and Poorly Understood Phenomena

The catalyst life is assumed to be 1 yr as reported by MKK in most instances. However, in the economics, MKK used a catalyst replacement period of 2 yr as a basis. There are also no statements by MKK on the effects of particulate levels >0.1 g/Nm³ (0.04 gr/sft³). There is no mention of materials of construction or maintenance requirements.

The maximum SO_x level tolerable by this catalyst is not available. MKK claims no adverse effects with a high SO_x level; however, the maximum level which has been tested apparently is 1000 ppm. The average level which can be expected for a coal-fired power plant flue gas is about 2400 ppm. The expected NH₃ level in the outlet gas has not been reported.

Advantages and Disadvantages

MKK's process has the following advantages and disadvantages.

Advantages

1. Achieves >90% NO_x removal efficiency
2. Uses catalyst which, when spent, has other potential applications

Disadvantages

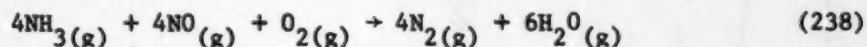
1. Has not been tested on coal-fired flue gas
2. Requires clean (indefinite level of particulate removal required) gas feed
3. Incorporates questionable design features (stacking of catalyst in reactor may be required)

MITSUBISHI PETROCHEMICAL PROCESS - DRY, SCR (NO_x)

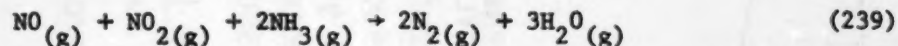
Process Description and Principles of Operation (54, 85)

Mitsubishi Petrochemical (MPC) is offering a highly efficient catalyst for the SCR of NO_x with NH₃. Although the company is not offering a process, the use of its catalyst would be the main difference among other dry SCR processes; therefore, it has been treated as a process in this review. The exact nature of the catalyst is not given by MPC but it is possibly a titanate as reported by Dr. Jumpei Ando (Chuo University, Tokyo, Japan).

With respect to NO, MPC states that with their catalyst the reduction of NO by NH₃ requires the presence of O₂ and that the reaction proceeds as follows:



With NO₂ present, the following reaction takes dominance over the preceding reaction, when the NO:NO₂ mol ratio exceeds 1:1.



The NH₃:NO_x ratio required is 1:1. The O₂ concentration and NH₃:NO_x ratio versus NO_x removal efficiency are shown in Figures 76 and 77.

There are three types of "PNX" catalysts manufactured by MPC for use at different conditions. PNX-A is suitable at high temperature and has a temperature range of 350-600°C (662-1112°F). Type B has application at low temperatures with a range of 300-450°C (572-842°F), while type C is used at temperatures in a range of 300-600°C (572-1112°F). At a space velocity of 10,000 hr⁻¹, each type is capable of NO_x removal of >95%. The estimated life is 1 yr for types B and C and 2 yr for type A. Types A and C are suitable at high SO_x concentrations (at least 2000 ppm) while B is suitable at 500 ppm SO_x.

Status of Development

MPC screened several hundred catalysts for use in an NO_x removal facility treating flue gas containing SO_x. A series of catalysts were developed which are more resistant to SO_x. Development is at the stage where the company can supply catalyst samples.

Background of Process Developer

Little information has been obtained on the background of MPC. However, MPC has a New York office making the catalyst more accessible to the U.S. market.

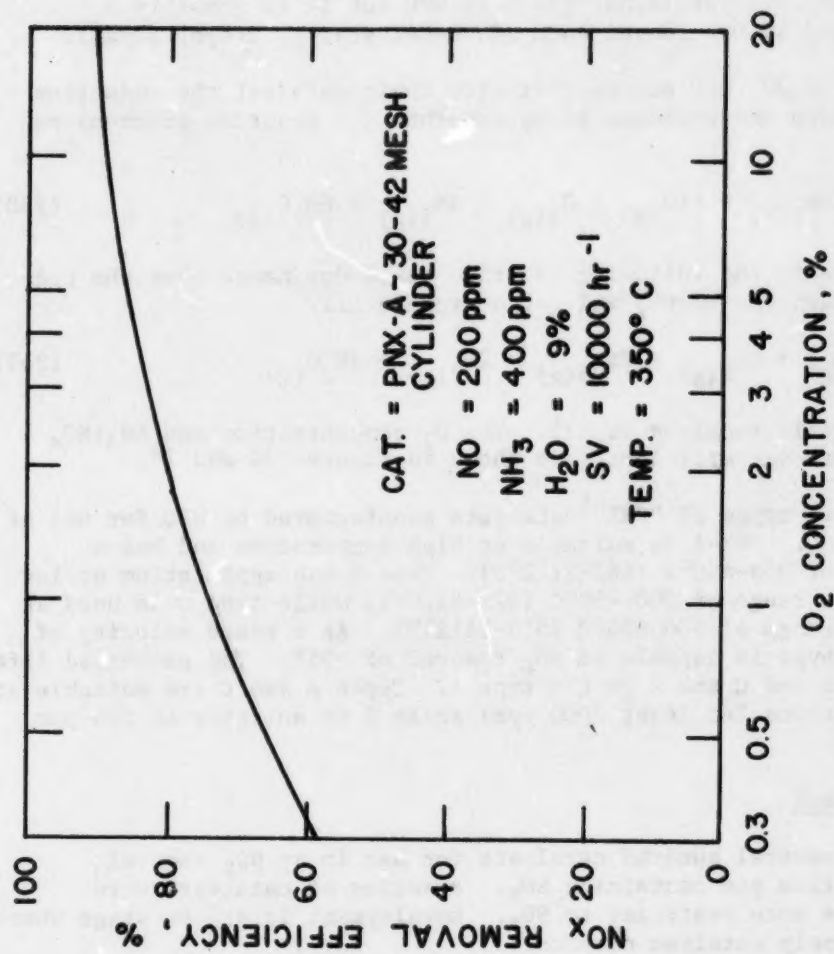


Figure 76. Effect of O₂ Concentration on NO_x Removal Efficiency with MPC Catalyst (54).

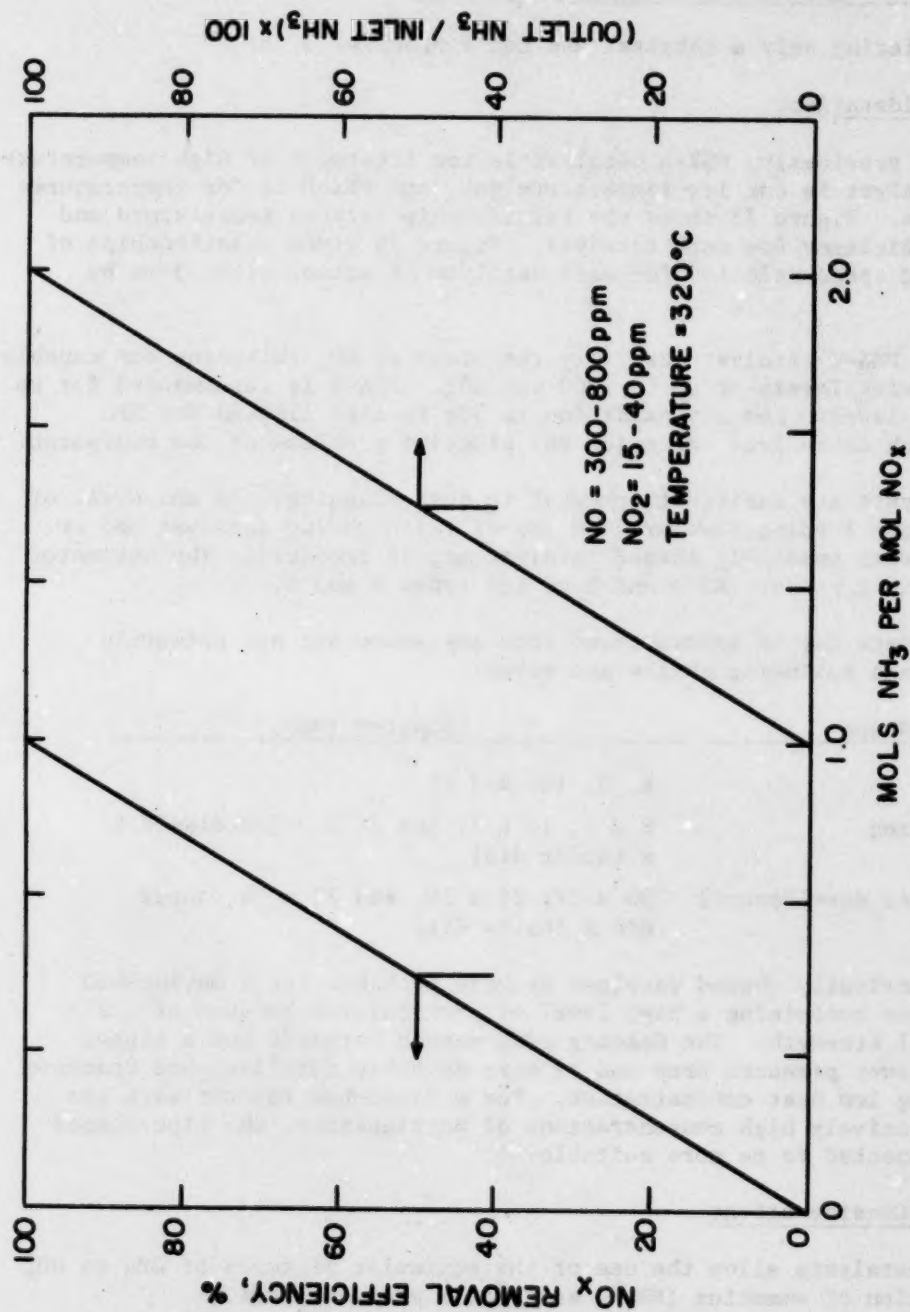


Figure 77. Effect of NH₃:NO_x Mol Ratio on NO Removal Efficiency with MPC Catalyst (85).

Published Economic Data

The cost of the catalyst is not reported by MPC.

Raw Materials, Energy, and Operation Requirements

MPC is offering only a catalyst and not a process

Technical Considerations

As stated previously, PNX-A catalyst is for treatment of high-temperature gas, PNX-B catalyst is for low-temperature gas, and PNX-C is for temperatures between the two. Figure 78 shows the relationship between temperature and NO_x removal efficiency for each catalyst. Figure 79 gives relationships of temperature and space velocity for each catalyst at actual size, 3 mm by 3 mm.

PNX-A and PNX-C catalysts are very resistant to SO_2 poisoning and capable of being used with levels of up to 2000 ppm SO_2 . PNX-B is recommended for up to 500 ppm SO_2 level. Low SO_2 oxidation to SO_3 is also claimed for MPC catalysts, which cause less corrosion and plugging problems of the equipment.

The catalysts are resistant somewhat to dust plugging. In the event of heavy particulate loading however, the use of (a) a moving catalyst bed or, (b) fixed bed with specially shaped catalyst may be required. The estimated catalyst life is 2 yr for PNX-A and 1 yr for types B and C.

The catalysts may be manufactured into any shape but are primarily designed into the following shapes and sizes:

Shape	Diameter (mm)
Cylinder	6, 8, 10, and 15
Raschig ring	8 x 4, 10 x 5, and 15 x 7 (outside dia x inside dia)
Pipe (under development)	30 x 22, 25 x 18, and 20 x 14 (outer dia x inside dia)

The cylindrically shaped catalyst is more suitable for a moving-bed reactor with gas containing a high level of particulates because of its higher physical strength. The Raschig ring-shaped catalyst has a higher activity and lower pressure drop and is more suitable for fixed-bed reactors with gas having low dust concentration. For a fixed-bed reactor with gas containing relatively high concentrations of particulates, the pipe-shaped catalyst is expected to be more suitable.

Environmental Considerations

The MPC catalysts allow the use of the equimolar mixtures of NH_3 to NO_x to keep formation of ammonium (NH_4^+) salts at a minimum level.

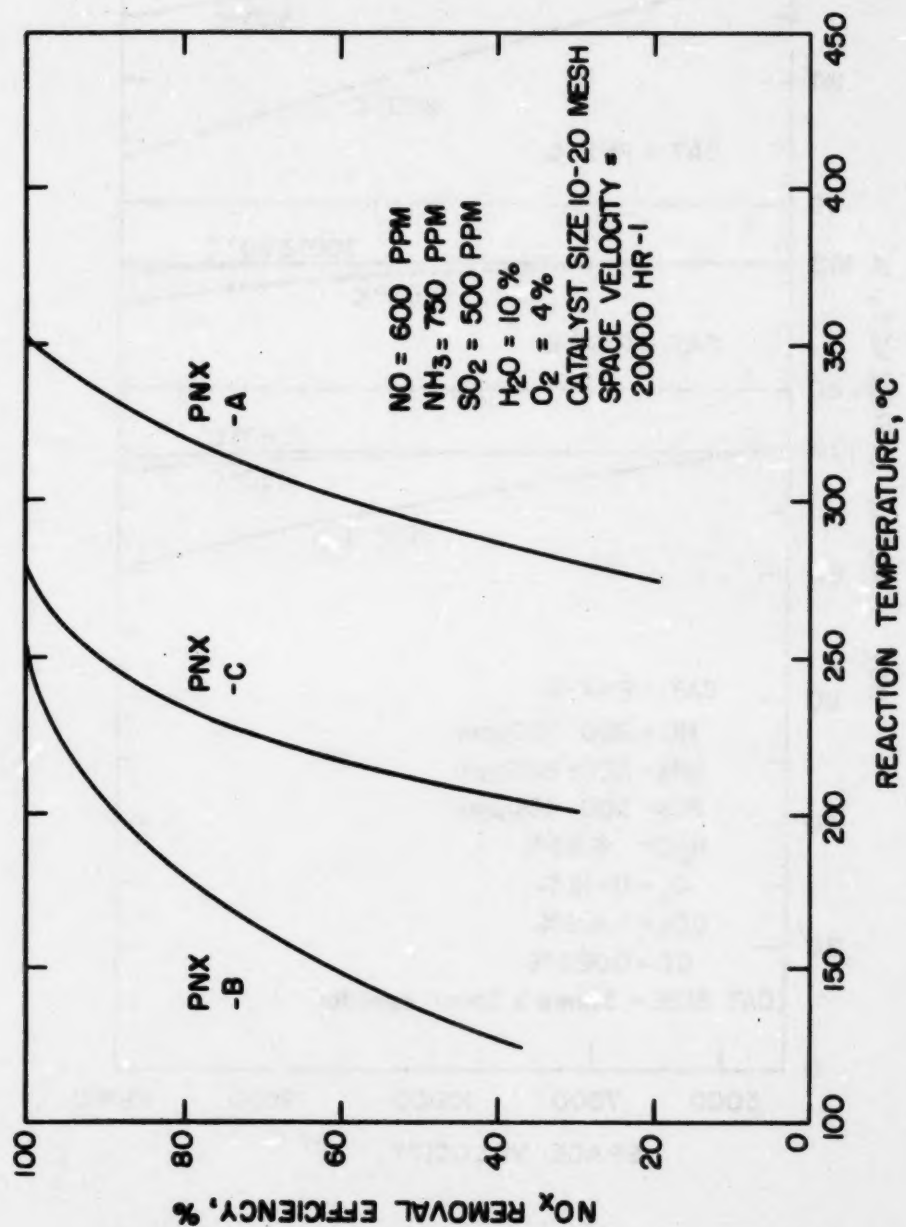


Figure 78. Effect of Temperature on NO_x Removal Efficiency with Various Types of MPC Catalysts (85).

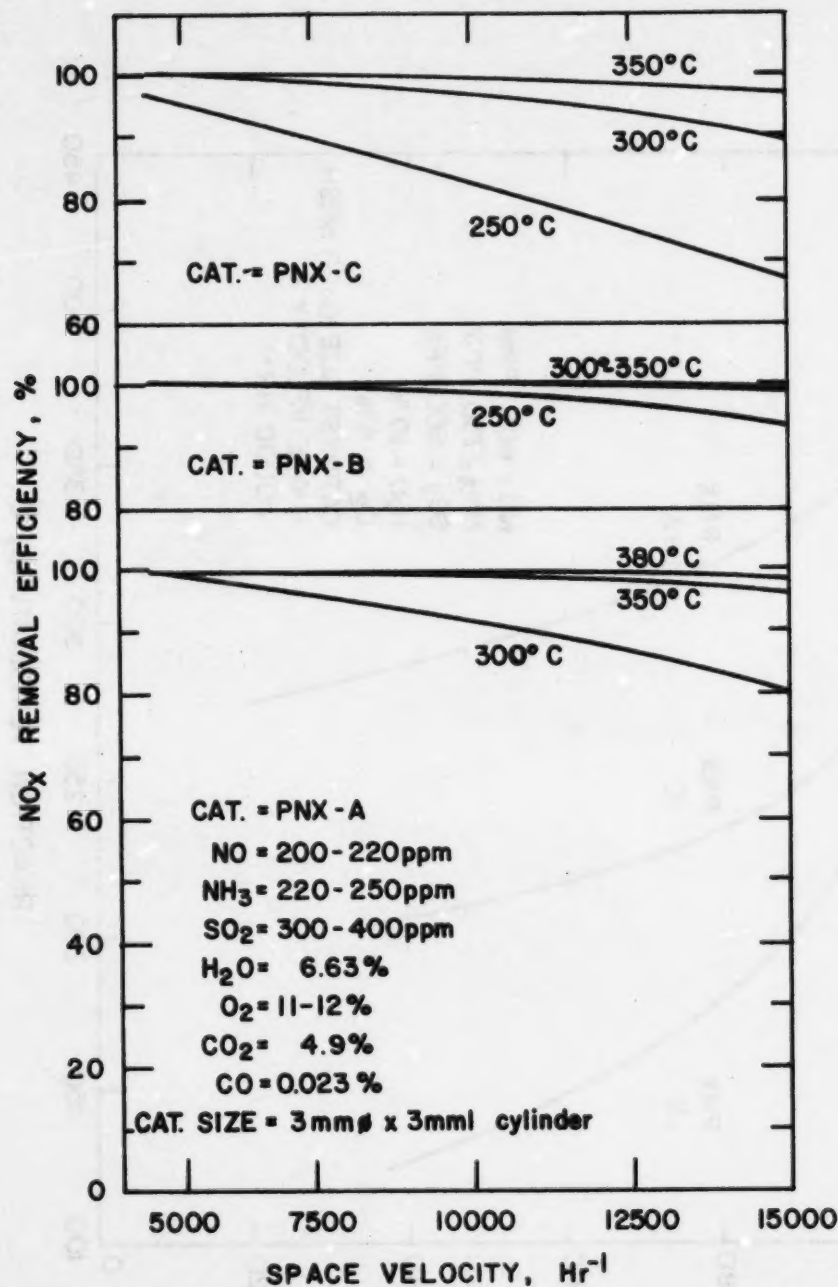


Figure 79. Relationship of NO_x Removal Efficiency to Temperature and Space Velocity for Various MPC Catalysts (54).

Critical Data Gaps and Poorly Understood Phenomena

The exact composition of the catalyst is unknown though it is said to be a titanate. There is also no mention of catalyst cost. Types A and C catalysts are applicable with flue gas containing up to 2000 ppm SO₂ and 60 ppm SO₃ but it is not stated if higher levels, such as 2400 ppm SO₂ with coal-fired boilers, are acceptable.

Advantages and Disadvantages

The advantages and disadvantages of the MPC catalysts are as follows:

Advantages

1. Achieves >90% NO_x removal efficiency

Disadvantages

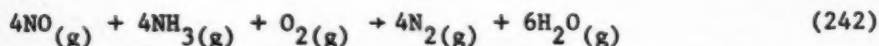
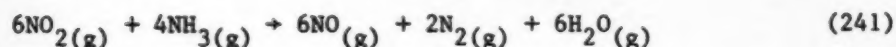
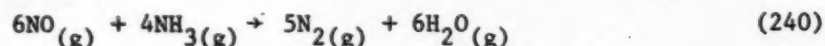
1. Has probably not been tested on coal-fired flue gas
2. Requires clean (indefinite level of particulate removal required) gas feed

MITSUI ENGINEERING AND SHIPBUILDING PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (16, 86)

The Mitsui (Mitsui Engineering and Shipbuilding Company, Ltd.,) dry process is an NO_x-only removal system based on the SCR of NO_x by NH₃. However, the Mitsui process can be tailored to fit the particular flue gas conditions at a specific site by inserting any one of three different types of catalysts (NXC-100, dust and SO_x free; NXC-200, dust-free; NXC-300, dirty gas) developed by Mitsui Petrochemical Industries, Ltd. Since only coal-fired gas is being considered in this study, the NXC-300 catalyst designed for heavy oil-fired flue gas will be considered. This dry SCR process is very similar to the other dry processes in that it consists of three distinct sections: particulate removal, NH₃ injection, and catalytic reduction. The basic outline for the Mitsui process can be seen from the block flow diagram given in Figure 80.

The flue gas from the economizer at 400°C (750°F) passes through a hot ESP to reduce the particulate levels below 0.2-0.4 g/Nm³ (0.09-0.17 gr/sft³ at 32°F) before entering the NH₃ mixing chamber. Gaseous NH₃ in an NH₃:NO_x mol ratio of (1.0-1.1):1 is injected and intimately mixed with the flue gas before entering the reduction reactor containing the proprietary base-metal catalyst. As the mixture passes through the packed-bed reactor at 350°C (660°F) the NO_x is selectively reduced to N₂ by the following reactions:



Since NO represents 90-95% of the NO_x in the flue gas, reactions (240) and (242) are the primary reactions occurring in the reactor.

The clean flue gas from the reactor passes through the boiler air heater and then the FGD section before exiting through the stack.

Status of Development

The Mitsui dry SCR process using the NXC-300 catalyst was initially tested in a bench-scale unit treating 200 Nm³/hr (0.06 MW equiv) of flue gas having the following composition: 1000 ppm SO₂, 300 ppm NO_x, 3% O₂, and 0.1-0.2 g/Nm³ dust. During a recent 6000-hr (250 day) continuous operation, the bench-scale unit was able to maintain 90% NO_x removal.

In October 1976 a pilot plant treating 5000 Nm³/hr (1.6 MW equiv) of flue gas (SO_x:1500 ppm, NO_x:150 ppm, and 0.2 g/Nm³ dust) from a 500-MW power plant burning heavy fuel oil was completed and began operating. During a 2300-hr (96 day) test, this pilot plant using the NXC-300 catalyst was able

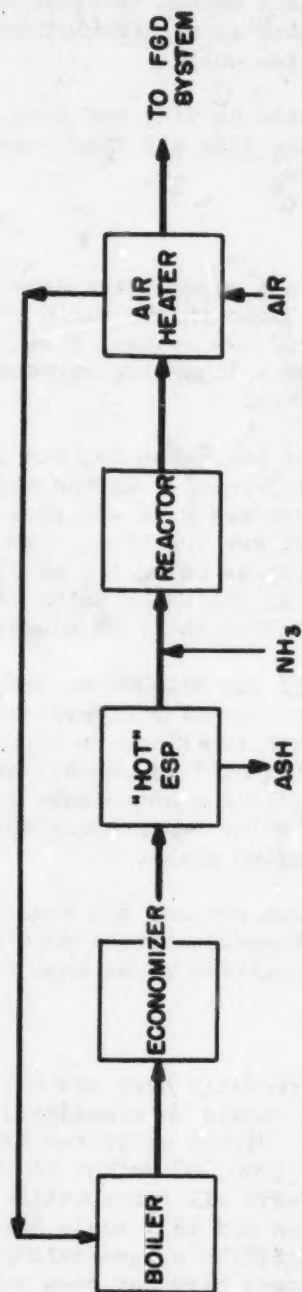


Figure 80. Flow Diagram of Mitsui Engineering and Shipbuilding Process.

to maintain 90% NO_x removal. In addition methods of preventing NH_4HSO_3 precipitation in the air heater downstream of the reactor are now being studied.

Recently the Mitsui process using the NXC-300 catalyst was selected by Mitsui Petrochemical Industries for a system to treat 200,000 Nm^3/hr (67 MW equiv) of flue gas from a heavy oil boiler. Preliminary plans indicate a July 1977 startup for this commercial unit.

This process has not been tested on flue gas from a coal-fired boiler, therefore, its ability to handle the flue gas from a coal-fired boiler needs to be evaluated.

Background of Process Developer

Mitsui is a relatively large and diversified Japanese corporation which entered the air pollution control field in the early 1970's. In addition to the development of their lime slurry FGD system, their early involvement in air pollution control also included a licensing agreement to build the Dowa $\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2\text{O}_3 - \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ FGD system.

In response to the adoption of stringent NO_x regulation in Japan, Mitsui began the development of their SCR process. In the initial testing of the Mitsui process, the NXC-100 catalyst was used and thus the testing was limited to flue gas containing neither dust nor SO_x (i.e., HNO_3 tail gas or natural gas-fired boilers). The Mitsui process using the NXC-100 catalyst was recently (October 1975) installed at the Chiba Works of the Mitsui Petrochemical and is treating 200,000 Nm^3/hr (66.7 MW equiv) of flue gas.

Two new catalysts, the NXC-200 and NXC-300 series, were developed by Mitsui Petrochemical. These two catalysts are more active than the NXC-100 series and, even more important, are resistant to SO_x . The NXC-200 series is specified for flue gas containing minimal amounts of dust and particulates while the NXC-300 series was designed for dust-laden gases. The NXC-300 series was first tested in a 200 Nm^3/hr bench-scale unit and in October 1976 began operating in a 5000 Nm^3/hr pilot plant.

At the present time no American company has been licensed by Mitsui to market this process in the U.S. However, Mitsui does have a liaison office in New York City, through which inquiries about this process are handled.

Published Economic Data

Since this process has only recently been tested in a pilot plant, the following published economic data should be considered as a preliminary estimate and subject to revision. Mitsui estimates (16) the total capital investment for a system to treat 1,000,000 Nm^3/hr of flue gas (corresponding to a 333-MW power plant) from a heavy oil-fired boiler as \$3,600,000 (assumed construction basis: Japan and 1976 costs but excluding foundation and civil work), or approximately \$10/kW of generating capacity. The annual revenue requirements for this process have not been published.

Raw Material, Energy, and Operation Requirements

The following raw material requirements were estimated by Mitsui based on a plant to remove 90% of the NO_x from $1,000,000 \text{ Nm}^3/\text{hr}$ (333 MW equiv) of flue gas. This inlet flue gas was from a heavy oil-fired boiler and was assumed to contain 170 ppm NO_x and 0.2 g/Nm^3 of dust.

<u>Material</u>	<u>Quantity required</u>
-----------------	--------------------------

NH_3	129 kg/hr
Catalyst	\$1.2M/yr

This catalyst cost is based on a 1-yr lifetime but recent information indicates that a 2-yr lifetime of the catalyst may be obtained and, hence, the catalyst cost could be substantially reduced. The utility requirements using the same basis were estimated as:

<u>Utility</u>	<u>Quantity required</u>
----------------	--------------------------

Steam	80 kg/hr
Cooling water	9 tons/hr
Electric power	2900 kW
Land	2500 m^2

This electrical requirement represents only 0.9% of the generating capacity of the boiler.

Essentially no operating manpower is required for this system since it is automated but occasional monitoring may be required. The maintenance requirements have not been published but are expected to be a minor cost.

Technical Considerations

The Mitsui process, as is typical for most dry, NO_x -only removal processes, is a relatively simple system with only five pieces of equipment: a hot ESP, an NH_3 storage tank, an NH_3 vaporizing tank, a mixing device, and the reduction reactor. The only major process control problem is vaporizing and injecting the exact amount of NH_3 required to provide an $\text{NH}_3:\text{NO}_x$ mol ratio of 1:1 in the reduction reactor. This NH_3 feed rate is controlled automatically by measuring both the flue gas rate and the concentration of NO_x in the gas.

The NO_x removal efficiency is relatively independent of the inlet flue gas providing the particulate levels are below 0.2 g/Nm^3 . Significantly higher particulate loadings and/or the presence of alkaline (i.e., Na, K, Zn, etc.) SO_3^{2-} or Cl^- in the flue gas will decrease the NO_x removal efficiency since they form a layer over the catalyst particles. The denitrification efficiency under normal operating conditions is completely independent of the H_2O , O_2 , and NO_x concentrations in the flue gas. As long as the temperature in the reactor remains near or above the recommended operating temperature of 350°C , the NO_x removal efficiency is insensitive to the flue gas

SO₂ concentration. If the temperature falls below 350°C, significant amounts of NH₄HSO₄ can form and plug the reactor and, thus, decrease the removal efficiency.

The catalytic reduction reactor will be the largest piece of process equipment and is apparently a packed-bed reactor. The catalyst particles are typically pipe shaped with diameters ranging from 5-50 mm and lengths of 300-1000 mm. These particle shapes are claimed to be highly resistant to dust. Although these catalyst particles are claimed to be highly active, the space velocity through the catalyst bed appears to be limited to approximately 5000 hr⁻¹ to guarantee 90% NO_x removal. However, even with dust levels of 0.1-0.2 g/Nm³ of dust, there was no increase in pressure drop with time during a 6000-hr test and it remained at about 100 mm of H₂O. Thus, for the purposes of this study, the operating conditions in the reduction reactor would be the following:

Parameter	Value
NH ₃ :NO _x mol ratio	1:1
Temperature	350°C (660°F)
Space velocity	5000 hr ⁻¹
Catalyst size-shape	5-50-mm-dia pipe
Dust level (max tested)	0.2 g/Nm ³

These operating parameters in the reduction reactor are very similar to those specified by the other SCR processes.

This process could not be easily retrofitted onto an existing 500-MW plant equipped with cold ESP. The ductwork modifications required to remove and return the flue gas between the economizer and the air heater would be extremely difficult and expensive. Thus, for retrofit applications, Mitsui recommends the flue gas be rerouted after the existing cold ESP and sent to a countercurrent heat exchanger where the raw flue gas extracts waste heat from the clean flue gas exiting the denitrification section. The flue gas is further heated in an oil-fired furnace to raise the temperature to 350°C (660°F) and then mixed with gaseous NH₃ before entering the reduction reactor. As the gas mixture passes through the reactor, the NO_x is catalytically reduced to N₂ and the effluent gas is sent to the heat exchanger to preheat the incoming raw flue gas before the clean gas enters the desulfurization section. Thus, the retrofitting of this system on existing power plants will increase both the capital investment and revenue requirements since extra equipment and fuel will be required.

Although Mitsui has suggested only one train of denitrification equipment needed for a 500-MW boiler, it is assumed from previous studies that two trains will be used with each train rated at slightly more than 50% of the boiler capacity. The use of two trains will allow the denitrification system to be better able to cycle with the boiler availability. The major consideration during turndown will be to maintain a high temperature (350°C) in the reactor area to prevent the formation and precipitation of NH₄HSO₄ on the reactor and catalyst surfaces.

There are no exotic materials of construction required for this process with all equipment made of carbon steel.

Environmental Considerations

The Mitsui process has been shown in bench-scale tests to be capable of selectively removing 90% of the NO_x by reaction with NH_3 . To maintain this high removal efficiency the temperature must remain above 350°C (660°F) and the mol ratio of $\text{NH}_3:\text{NO}_x$ must remain at approximately 1:1. At lower temperatures, NH_4HSO_4 will form on the catalyst surface and the NO_x removal efficiency will quickly drop below 90%. When less than the specified amount of NH_3 is injected, the denitrification efficiency will also decline below 90%.

This process is designed specifically for the selective removal of NO_x and does not remove any other pollutants from the flue gas.

The only major source of secondary pollution from this system will be NH_3 emissions in the flue gas. These emissions are expected to be about 60 ppm and they may present a significant problem since, as the flue gas is cooled, NH_4HSO_4 could be formed. However, Mitsui is currently conducting pilot-plant tests to minimize NH_3 emissions and associated problems.

Critical Data Gaps and Poorly Understood Phenomena

The critical data gaps for this process involve the operating requirements and costs for this system. Mitsui has not as yet published any information on the annual operating costs and maintenance requirements.

Advantages and Disadvantages

Advantages and disadvantages for the Mitsui process are listed below:

Advantages

1. Achieves >90% NO_x removal efficiency

Disadvantages

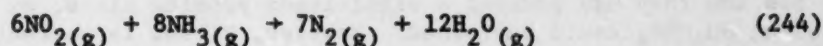
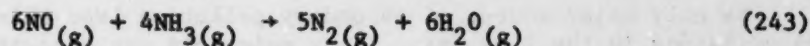
1. Forms secondary source of pollution (NH_3 level in outlet gas may be 60 ppm)
2. Has not been tested on coal-fired flue gas
3. Requires somewhat clean (particulate level $<0.1\text{--}0.2\text{ gr/sft}^3$ needed before reactor) gas feed

MITSUI TOATSU CHEMICALS PROCESS - DRY, SCR (NO_x)

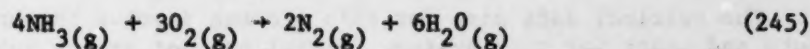
Process Description and Principles of Operation (41, 87)

Mitsui Toatsu Chemicals, Inc., (MTC) is developing an SCR NO_x removal process. The NO_x is converted to N₂ and H₂O by NH₃ in the presence of a catalyst.

Based on a process flow scheme from MTC for dirty gas treatment, an assumed flowsheet for NO_x removal at a coal-fired power plant is given in Figure 81. After the flue gas passes from the boiler and through the air heater, NH₃ is injected into the flue gas stream. The flue gas is then heated to the required temperature range of 350°-400°C (662-752°F) by passage through a heat exchanger and through the use of an auxiliary heater. Then the flue gas has the particulates removed, for example, by a hot ESP, and then enters the reactor. In the reactor in the presence of the catalyst, the following reactions occur, as reported by MTC:



MTC also states that the excess NH₃ is decomposed to N₂ and H₂O by the following reaction:

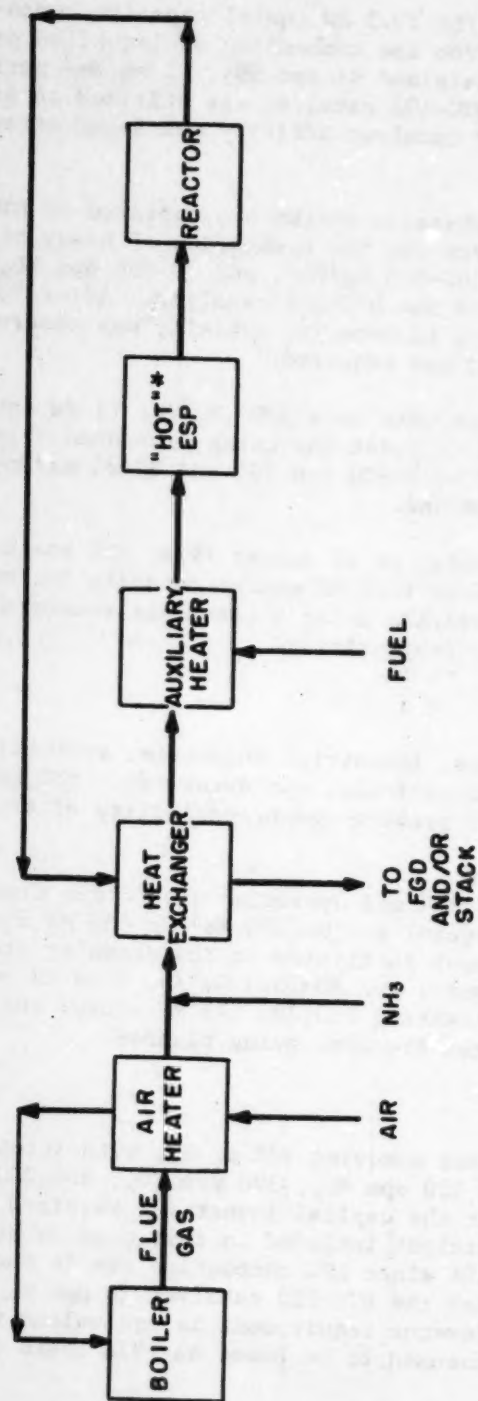


The treated flue gas is sent through the heat exchanger to transfer the heat to the untreated flue gas flowing to the reactor. Upon exiting the heat exchanger, the treated flue gas is sent to an FGD unit and/or the stack.

The NH₃:NO_x mol ratio used ranges from 0.9:1-1.2:1. The reaction temperature is 350-400°C (662-752°F) and the applicable space velocity varies from 3,000 hr⁻¹ to 10,000 hr⁻¹. The reactor would incorporate either an intermittent moving-bed or a fixed-bed with a honeycombed-structured catalyst. NO_x removal of >90% is reported.

Status of Development

MTC states that five different catalysts, divided into groups composed of Cu, Fe, or V, have been developed and are commercially available. MTC-102 catalyst (Cu catalyst group) is suitable for treating clean flue gas containing <1 ppm SO_x and 1 mg/Nm³ of dust at temperatures from 200-280°C. In addition to this clean gas treatment, MTC-104 and MTC-108 catalysts (Fe and V catalyst groups respectively) may also be used in treating flue gas from crude oil and naphtha combustion which contains 100 ppm SO_x. The temperature ranges required are 300-450°C for MTC-104 and 200-380°C for MTC-108. MTC-110 catalyst (V group) must be used with flue gas containing very much SO_x and



* ASSUMED NECESSARY FOR COAL-FIRED POWER PLANT

Figure 81. Flow Diagram of Mitsui Toatsu Chemicals Process.

dust, such as fuel oil combustion gas. MTC-110 is used at temperatures of 270°C to 400°C and may be used at SO_x concentrations of at least 1,000 ppm.

MTC has operated a 1,000 Nm³/hr (0.3 MW equiv) capacity bench-scale unit at its Osaka plant on clean gas from the combustion of liquefied propane gas (LPG). The inlet flue gas contained <1 ppm SO₂, <1 mg/Nm³ particulates, and about 200-300 ppm NO_x. The MTC-102 catalyst was utilized to achieve >90% NO_x removal. No decrease in catalyst activity was found after 7,000 hr of continuous operation.

A 1,000 Nm³/hr capacity bench-scale system was operated by MTC at its Chiba plant and the flue gas source was the combustion of heavy oil. The flue gas contained 100 ppm SO₂, 100-300 mg/Nm³, and 30-150 ppm NO_x. The NO_x removal achieved was >90% with the MTC-104 catalyst. After 5000 hr of continuous operation, no reduction in catalyst activity was observed. Particulate removal before the reactor was required.

The MTC-104 catalyst was also used on a 3000 Nm³/hr (1 MW equiv) capacity pilot plant at MTC's Osaka plant to treat gas being exhausted from an FGD unit. The flue gas was composed of 10-20 ppm SO₂ and 50-80 mg/Nm³ particulates. NO_x removal >90% was obtained.

In addition to the above tests, as of August 1976, MTC has been operating 4000 (1.3 MW equiv) and 8200 Nm³/hr (2.7 MW equiv) capacity NO_x removal facilities. These have been operating using a clean gas source since September 1974 and June 5, 1975, respectively.

Background of Developer

MTC manufactures fertilizers, industrial chemicals, synthetic resins and plastics, pesticides, pharmaceuticals, and dyestuffs. MTC has liaison offices in New York which should promote the accessibility of this process to the U.S. market.

NO_x removal plants constructed and operating with clean flue gas as late as 1976 include 84,000 (28 MW equiv) and 90,000 Nm³/hr (30 MW equiv) capacity plants. Other clean gas treatment facilities in the planning stages (as of 1976) include 220,000 (73 MW equiv) and 300,000 Nm³/hr (100 MW equiv) size units. Facilities capable of treating 230,000 (77 MW equiv) and 250,000 Nm³/hr (83 MW equiv) of dirty gas are also being planned.

Published Economic Data

For a 67-MW equiv size plant removing 90% of NO_x with inlet flue gas from LPG combustion containing 100 ppm NO_x, 300 ppm SO_x, and 200 mg/Nm³ of dust, it is estimated (87) that the capital investment required is \$3.3M, which is about \$49/kW. The catalyst included in this cost is not stated but may be either MTC-102 or MTC-104 since LPG combustion gas is the flue gas source. It should be noted that the MTC-110 catalyst is two to three times more expensive than MTC-104. The revenue requirement is equivalent to 1.6 mills/kWh (87). These figures are assumed to be based on 1976 costs and a Japanese location.

Raw Material, Energy, and Operation Requirements

The raw materials and energy requirements for denitrification have not been obtained. It may be estimated, however, for the 67-MW equiv- NO_x removal unit treating flue gas with 100 ppm NO_x , that 0.5 short tons/day of NH_3 are needed assuming an $\text{NH}_3:\text{NO}_x$ mol ratio of 1.1:1 is applied. Data covering operating manpower, maintenance, and technical support have not been released.

Technical Considerations

The MTC method is similar to other dry NO_x removal processes in its technical aspects. Though not stated by MTC, the NH_3 flow will probably be automatically controlled based on the NO_x content in flue gas and the reactor temperature will be maintained automatically by the auxiliary heater.

The reactor is the largest piece of equipment and should be the same or slightly larger in size as compared to similar dry methods. Since the reaction temperature is exactly the same as required by most SCR processes (350-400°C), the comparative size of the reactor will depend on the maximum allowable space velocity, which ranges from 3,000 to 10,000 hr^{-1} .

MTC has operated NO_x removal units with fixed-bed reactors containing pellet-shaped catalyst and intermittent moving-bed reactors with spherical-shaped catalyst. The fixed-bed reactor is most suitable for handling flue gas with very low levels of particulate matter, such as LNG- or LPG-fired flue gas. Intermittent moving-bed reactors have been employed with crude oil, naphtha, and fuel oil combustion gases. The catalyst bed is moved as the particulates accumulate on the catalyst to have the dust accumulation blown away. MTC is currently studying a honeycomb-shaped catalyst structure for use in a fixed-bed reactor and is searching for the optimum method for treating coal-fired flue gas.

This process as described in the flow diagram can be retrofitted into an existing power plant. For the process shown, large amounts of reheat are required and thus heating and heat exchange equipment are needed. Naturally, more reheat would be necessary if this system had to be retrofitted after an FGD system than if placed only after a cold ESP or ahead of an FGD unit. As true for other dry processes, this MTC system would prove much more economical if it were possible to operate before the air heater.

A number of separate NO_x reduction trains will be needed for a 500-MW boiler. The major turndown capability will be the closing off of any combination of trains as required by boiler load variations. If an auxiliary heater is used, this would provide some reactor temperature control capability during boiler load fluctuations.

No information is presently available on materials of construction and sensitivity of denitrification to inlet gas composition.

Environmental Considerations

The MTC process reduced more than 90% of the NO_x in the flue gas during pilot-plant tests. This efficient NO_x removal was achieved with $\text{NH}_3:\text{NO}_x$ mol ratio between 1:1 and 1.2:1, reactor temperature of about 350-400°C, and a space velocity between 3,000 and 10,000 hr^{-1} . The effects of components such as SO_2 and Cl^- at levels expected to be found in coal-fired flue gas have not been made available. The highest known SO_2 level tested at present is about 1000 ppm SO_2 . It is reported by MTC that the NH_3 in the treated gas is capable of being controlled at ≤ 5 ppm.

This system only removes NO_x and does not eliminate any other pollutants from the flue gas.

Critical Data Gaps and Poorly Understood Phenomena

Information not presently obtained from MTC for this process includes the following items:

- a. Specifics on reactor design and maximum expected pressure drop
- b. Maximum tolerable SO_x level in the inlet flue gas
- c. Sensitivity of NO_x removal to inlet gas composition and $\text{NH}_3:\text{NO}_x$ mol ratio
- d. Raw material and catalyst consumption and utility requirements
- e. Operating manpower and maintenance requirements
- f. Materials of construction
- g. Catalyst composition and availability

Advantages and Disadvantages

The advantages and disadvantages of the MTC process are as follows:

Advantages

1. Achieves >90% NO_x removal efficiency
2. Claims <10 ppm by vol NH_3 in treated flue gas

Disadvantages

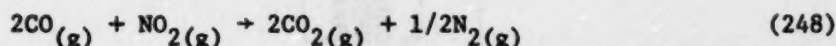
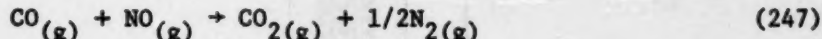
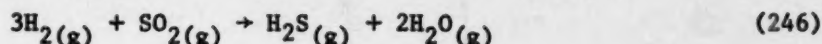
1. Has not been tested on coal-fired flue gas
2. Requires clean (degree of particulate removal required is uncertain) gas feed
3. Uses moving-bed reactor which increases maintenance and catalyst attrition
4. Requires auxiliary heater to attain or control reaction temperature

THE RALPH M. PARSONS COMPANY PROCESS - DRY, NONSELECTIVE CATALYTIC
REDUCTION (NO_x-SO_x)

Process Description and Principles of Operation (31, 32)

This flue gas denitrification system being developed by The Ralph M. Parsons Company is a dry catalytic reduction process in which both the SO₂ and the NO_x are nonselectively reduced in the presence of a catalyst in a single step. However, this process is fundamentally different from any of the other flue gas denitrification schemes discussed in this study. Instead of consuming expensive NH₃ to selectively reduce the NO_x as in the other dry NO_x removal processes, the operating conditions in the boiler are modified such that a neutral or slightly oxidizing atmosphere is maintained in the boiler. This boiler atmosphere would be obtained by a combination of holding the excess air in the boiler to a minimum and the injection of a hydrocarbon fuel, such as natural gas or producer gas, into the radiant zone of the boiler. This will minimize the amount of free oxygen remaining in the flue gas and thus reduce the formation of SO_x and NO_x.

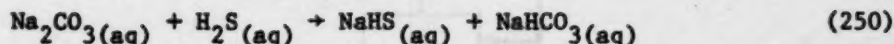
The flue gas from the boiler passes through a hot ESP in which 99% of the particulates are removed and is then sent to a catalytic reduction reactor containing an inexpensive, nonnoble metal catalyst. A simplified flow diagram of the process is shown in Figure 82. The SO₂ is converted to hydrogen sulfide (H₂S) and the NO_x is reduced to N₂ by the following hypothesized reactions:



In addition to these primary reactions, other secondary reactions are catalyzed including the conversion of CO to CO₂ and also the conversion of both COS and carbon disulfide (CS₂) to CO₂ and H₂S.

The flue gas from the reduction reactor passes through the boiler air heater and through a Stretford absorber to remove the H₂S before the flue gas is reheated and exits through the stack.

As the flue gas passes through the Stretford tower, the H₂S is absorbed by a Na₂CO₃ solution and forms sodium hydrosulfide (NaHS) by the following reactions:



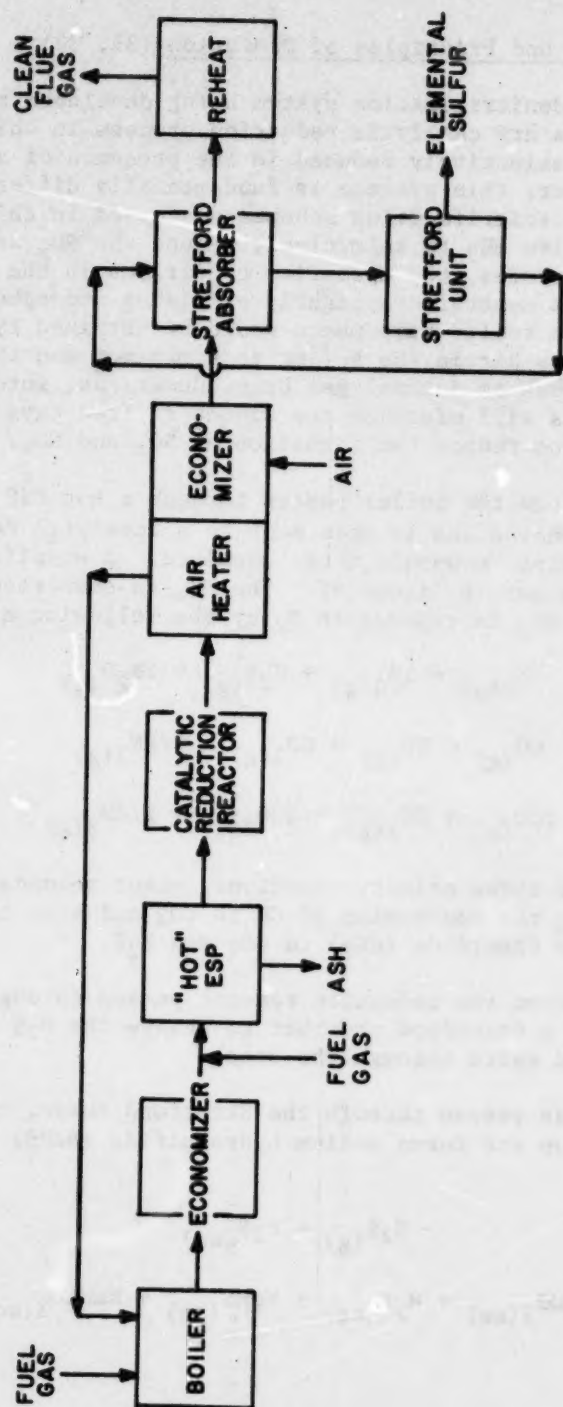
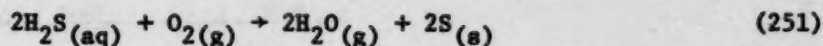


Figure 82. Flow Diagram of The Ralph M. Parsons Company Process.

Through a complex sequence of reactions involving soluble V compounds, this hydrosulfide ion (HS^-) is reduced to byproduct S. The overall reaction, however, is written as simply:



Status of Development

The Ralph M. Parsons process is in a conceptual design stage and has not been tested in a bench-scale unit. However, this process utilizes in part, technology previously developed jointly by the Union Oil Company and The Ralph M. Parsons Company during commercialization of the Beavon S removal process.

This process has not been demonstrated on coal-fired flue gas.

An appropriate next stage in the development of this process would be the demonstration of this system in a bench-scale unit treating actual power plant stack gas (preferably coal-fired flue gas).

Background of Process Developer

The Ralph M. Parsons Company is a well-known international engineering-construction firm based in Pasadena, California. In addition to an overall involvement in the design of petrochemical and chemical, power generation, and metallurgical facilities, Ralph M. Parsons is particularly well known for their design of S recovery plants for treating acid gases.

Their Beavon process was originally developed jointly with Union Oil Company to upgrade the SO_2 recovery of the Claus process to meet the more stringent environment regulations now being applied for SO_x . The first commercial Beavon unit (for S removal only) was completed in 1973 and 21 commercial units are currently operating.

This simultaneous SO_2 - NO_x removal process was originally conceived, in the early 1970's, during the development of the Beavon process. Supplemental development work, other than the conceptional design data, has not been completed. This simultaneous SO_2 - NO_x process has not been demonstrated either in a bench-scale or a pilot-plant unit.

Published Economic Data

The Ralph M. Parsons Company has estimated costs (32) for three different treatment systems depending on the method of generating the reducing atmosphere. For the purposes of this study, case 1 will be for a system with the simple injection of hydrocarbon fuel (natural gas) into the radiant zone of a new 500-MW boiler and case 2 will be for a system using an auxiliary boiler to generate the required amount of reducing gas for a new 500-MW boiler. Also, a third case based on retrofitting the system on an existing 225-MW boiler is included. In each case the resulting flue gas is passed through the same catalytic conversion section to convert SO_2 to

H₂S and NO_x to N₂. The costs of each of the three cases given below are approximate costs, based on a U.S. construction site and mid-1972 dollars.

	Case 1	Case 2	Case 3
	500-MW	500-MW	225-MW
	new	new	retrofit
Total capital investment			
\$	10,380,000	10,843,000	7,972,000
\$/kW	20.75	21.69	35.43
Annual revenue requirements			
\$/yr	2,932,000	3,501,000	2,170,000
Mills/kWh	0.84	1.00	1.38

Raw Material, Energy, and Operation Requirements

The following raw material requirements were estimated by Ralph M. Parsons for a new 500-MW coal-fired unit (coal analysis: 3.6% S, 9.0% ash, 12,600 Btu/lb heating value) based on case 1 where fuel is injected into the radiant zone of the boiler.

Raw material	Quantity
Natural gas	13,000 sft ³ /min
Catalyst and chemicals	Not available

The utility requirements on the same basis given above are:

Utility	Quantity
Electricity	3,940 kW
H ₂ O	115 gpm
Steam	2,500 lb/hr

The only byproduct of this system is elemental S which is of marketable quality. On the basis given above, about 4.73 long tons of elemental S per hour will be produced.

The operating manpower needed for this system is about two men per shift.

Technical Considerations

The process equipment needed for the simple fuel injection case is minimal except for the Stretford unit. The major process control problem for this case would be to inject the required amount of fuel into the boiler since the addition of too much fuel would result in a reducing atmosphere in the boiler. This reducing atmosphere could create major corrosion problems in the boiler as well as increased operating costs for the process. On the other hand, the injection of less than the optimum amount of fuel would result in higher levels of S and NO_x in the flue gas and would lower both the desulfurization and the denitrification efficiencies.

The SO_2 and NO_x removal efficiencies are dependent on the inlet flue gas conditions since the flue gas must not contain any free O_2 at the catalytic reduction reactor and must contain an excess of reducing gases such as H_2 or CO . The presence of O_2 in the flue gas will consume the reducing gas preferentially with the result that neither the SO_2 or the NO_x will be reduced. The effects of the particulates in the coal-fired flue gas on the catalyst and, hence, the removal efficiencies of both S and NO_x , are unknown, but can be expected to complicate the catalytic reduction reactor.

The conversion of SO_x to H_2S in the reduction reactor allows better waste heat recovery from the flue gas since the problem of H_2SO_4 formation is eliminated. A secondary economizer can be added after the boiler air heater to cool and recover heat which is normally lost due to the presence of SO_3 and H_2O in the flue gas. As an additional benefit of this conversion of SO_2 to H_2S and its subsequent removal, the process developers believe that the flue gas reheat step may not be required.

With impending shortages and higher prices of natural gas, the injection of natural gas into the boiler to consume the free O_2 and generate a neutral atmosphere is probably not a viable alternative. An alternative scheme suggested by Ralph M. Parsons would be to use vaporized fuel oil or an auxiliary boiler operating at substoichiometric air to generate a reducing gas which would then be injected before the reduction reactor. Either of these alternatives would have to be used in conjunction with both boiler modifications to sharply reduce excess air to the primary boiler and with the injection of some of the reducing gas into the primary boiler to remove any remaining free O_2 . (The economics for this system are given as case 2 in the section, Published Economic Data.) A block flow diagram for this system is given in Figure 83.

Although the sizes of the various pieces of process equipment have not been made available, there is no exceedingly large or exotic equipment needed for this process. The Stretford absorber and regeneration equipment are expected to be the only major pieces of process equipment. However, these Stretford units are used in commercial applications.

This process is expected to require two separate trains connected by a common plenum from the boiler, each rated at 56% of the total boiler capacity. By shutting down either of the trains, the system can provide a reasonable turndown capability.

For retrofit applications, The Ralph M. Parsons Company recommends an auxiliary boiler to generate the reducing gas to be injected before the catalytic reduction reactor. Other modifications and technical considerations have not been made available.

The process developers do not expect any change in the materials of construction in the boiler. The catalytic reduction section and the Stretford section will be constructed of carbon steel.

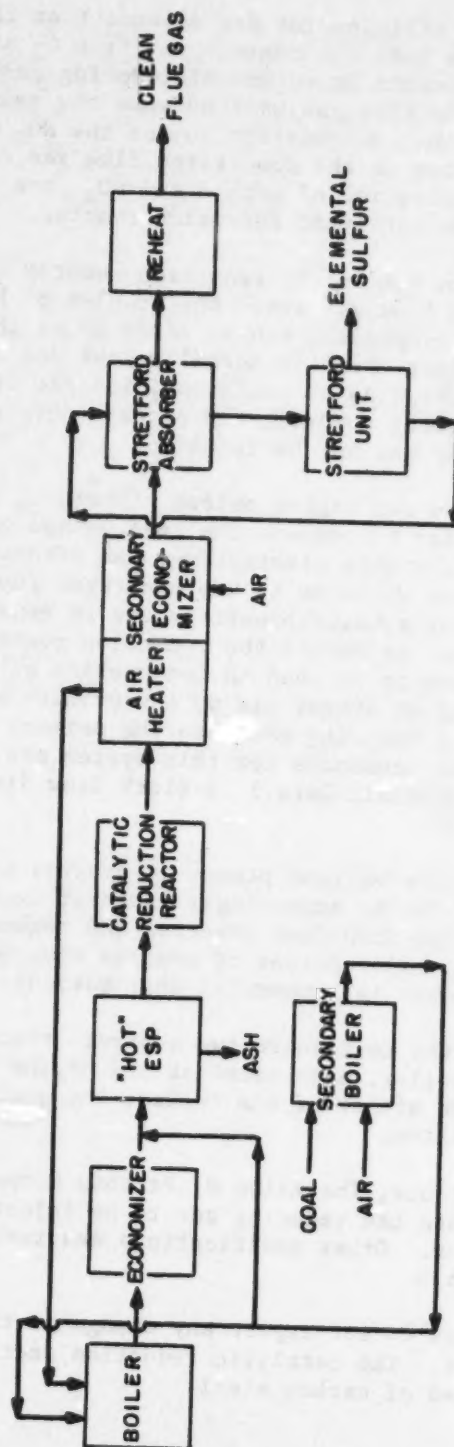


Figure 83. Flow Diagram of Alternative Ralph M. Parsons Process.

Environmental Considerations

Since the NO_x is reduced to N_2 and the SO_x is removed as elemental S, there are no apparent waste disposal problems associated with this process.

The generation of a reducing atmosphere in this system will result in the formation of several toxic gases including CO, H_2S , and COS which should be considered as a work hazard. However, with a properly designed system and the extensive experience of The Ralph M. Parsons Company in treating such gas streams, the risks associated with these gases can be minimized.

Critical Data Gaps and Poorly Understood Phenomena

Although this process as applied to boilers is only in the conceptual design stage and only a minimum amount of information is available, the following critical data gaps have become apparent:

1. Operating conditions in the various parts of the system
2. Design of the catalyst reduction reactor and catalyst particles
3. Effect of particulates and SO_3 on the catalyst
4. The effect of introducing a reducing atmosphere in the high temperature section of the boiler.
5. Expected SO_2 and NO_x removal efficiencies

Unfortunately at this stage of development many of these questions cannot be answered. Further studies will be required to investigate many of these critical data gaps.

Advantages and Disadvantages

Advantages and disadvantages of the Ralph M. Parsons process are listed below. Additional advantages and disadvantages may become apparent as development work progresses beyond the conceptual design stage.

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Produces marketable byproduct (S)

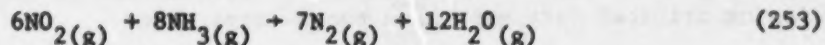
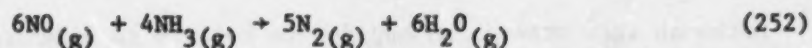
Disadvantages

1. Has not been tested on coal-fired flue gas
2. Has not been developed beyond the conceptual design stage
3. Requires somewhat clean (degree of particulate removal required is uncertain) gas feed
4. Incorporates design features which may present significant process control problems
5. Requires flue gas reheat for plume buoyancy

SUMITOMO CHEMICAL PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (4, 5, 90, 91, 101)

Sumitomo Chemical Company, Ltd., has developed a dry, SCR method for removing NO_x from flue gas. Treatment for a dirty gas would include the steps shown by the block flow diagram in Figure 84. The flue gas from the boiler passes through an air heater, an ESP for particulate removal, and then a heat exchanger and auxiliary heater to be heated to reaction temperature of about 350°C (662°F). NH₃ is introduced into the flue gas after the auxiliary heater and before the gas enters the reactor. In the reactor, the NO_x is reduced to N₂ by NH₃ in the presence of an SO_x-resistant catalyst according to Sumitomo by the following reactions:



The treated gas exits the reactor, passes through the heat exchanger to heat the untreated flue gas going to the auxiliary heater, and then proceeds to a desulfurization unit and/or the stack.

The average operating conditions and removal efficiency for dirty gas are as follows:

Reaction temperature	350°C (662°F)
NH ₃ :NO _x mol ratio	1:1
Space velocity	10,000 hr ⁻¹
NO _x removal efficiency	90%

Status of Development

Sumitomo Chemical has conducted many investigations on NO_x removal with pilot plants. It is reported that testing more than a thousand catalysts in clean and dirty flue gas led to the development of a base metal oxide carried on Al₂O₃ as the most suitable catalyst. A prototype unit of 30,000 Nm³/hr (10 MW equiv) gas capacity for treatment of an oil-fired flue gas has been operated since July 1973. Large commercial units for both gas and oil-fired flue gas are also in operation (see Background of Process Developer). Figure 85 indicates relationships of temperature and NH₃:NO_x mol ratio to NO_x removal efficiency for catalyst C-1 on clean gas. (Results are discussed in greater detail under Environmental Considerations.) A catalyst (A) for decomposing excess NH₃ was also developed and its effect with C-1 catalyst at 350°C (662°F) is shown in Figure 86. As can be noted, there is <10 ppm NH₃ in the outlet gas even with an NH₃:NO_x ratio of 1.5:1. Sumitomo stated that the NO_x removal efficiency increased about 5% with the use of catalyst A. Figure 87 indicates that catalyst D which was produced to resist SO_x is not significantly affected by SO₃ while catalyst C-1 is adversely affected. The relationship of concentration of each of NH₃ and SO₃ to the NH₄HSO₄ formation

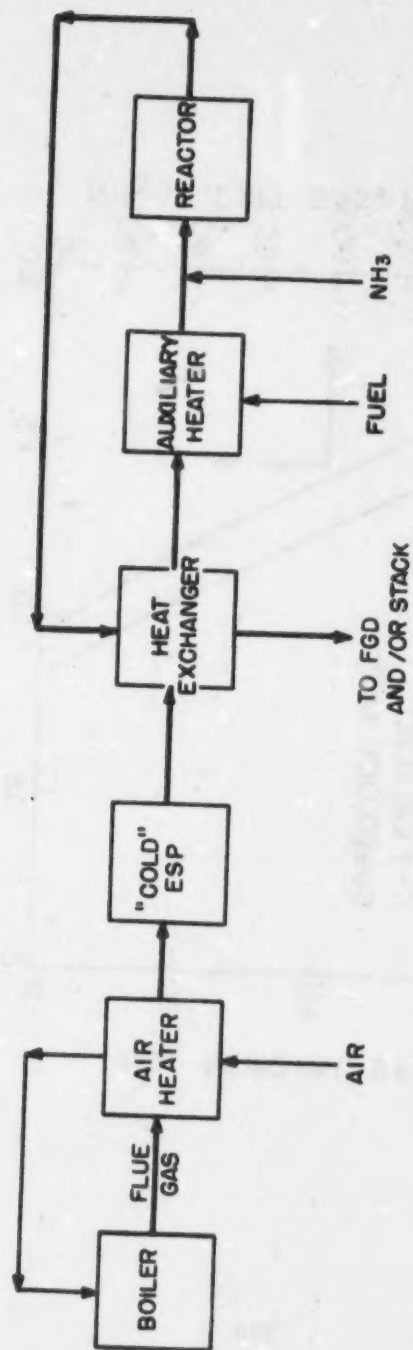


Figure 84. Flow Diagram of Sumitomo Chemical Process.

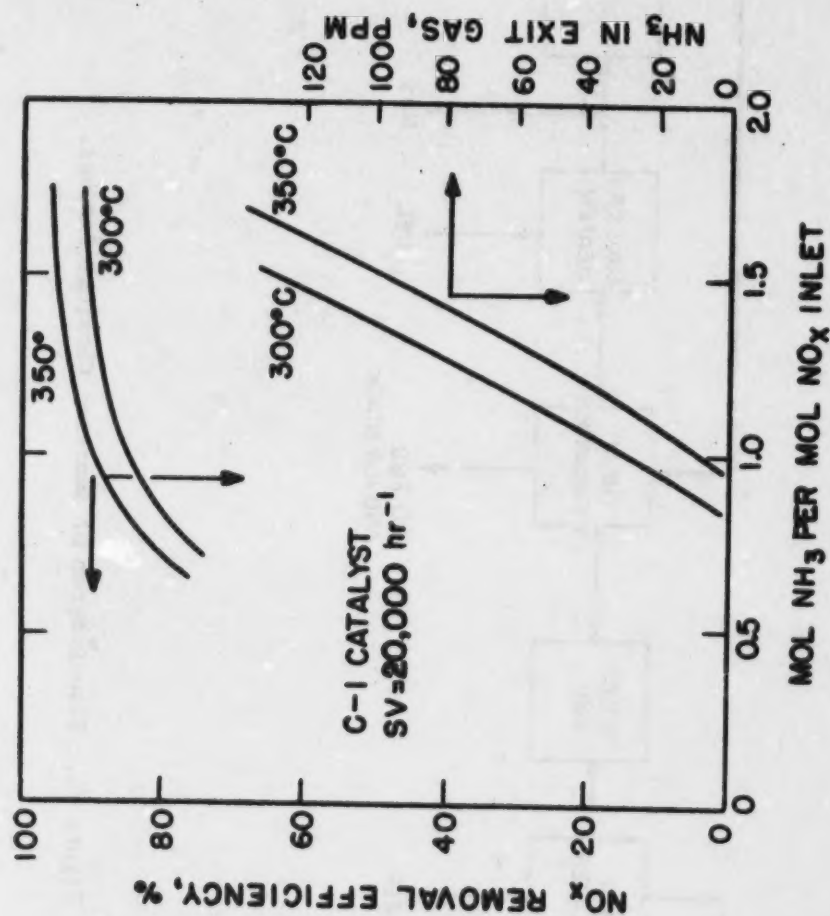


Figure 85. Relationship Among Inlet NH_3 : NO_x Mol Ratio, NO_x Removal Efficiency, and Exiting NH_3 Concentration Using the Sumitomo Chemical C-1 Catalyst (91).

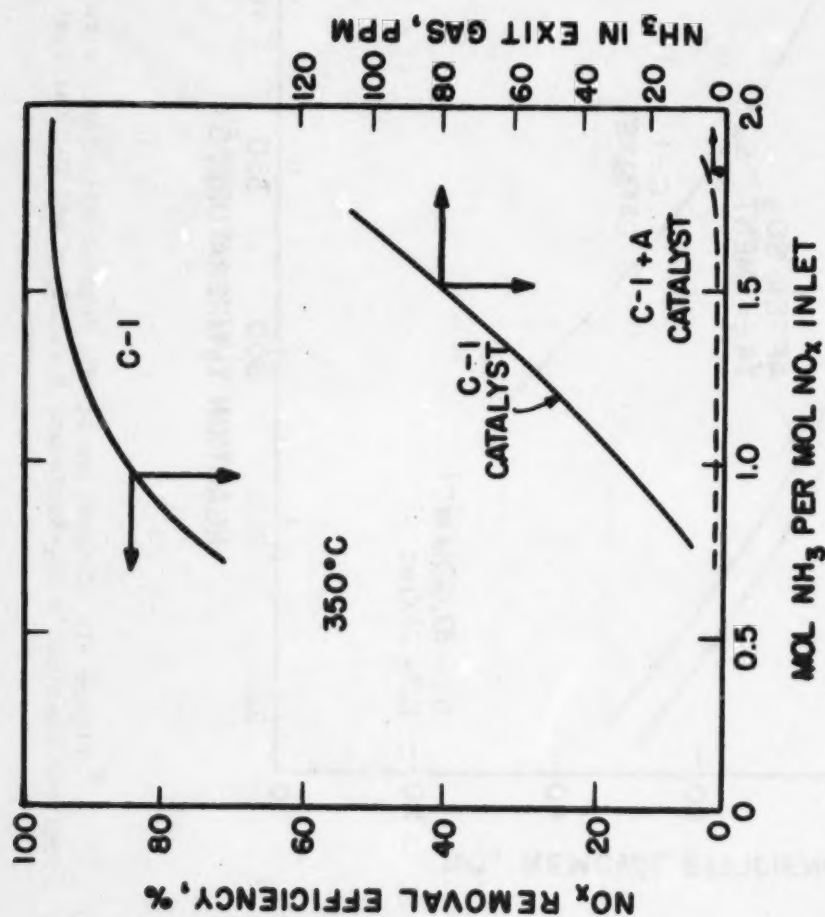


Figure 86. Relationship Among Inlet $\text{NH}_3:\text{NO}_x$ Mol Ratio, NO_x Removal Efficiency, and Exiting NH_3 Concentration Using an NH_3 Decomposition Catalyst with the C-1 Catalyst (101).

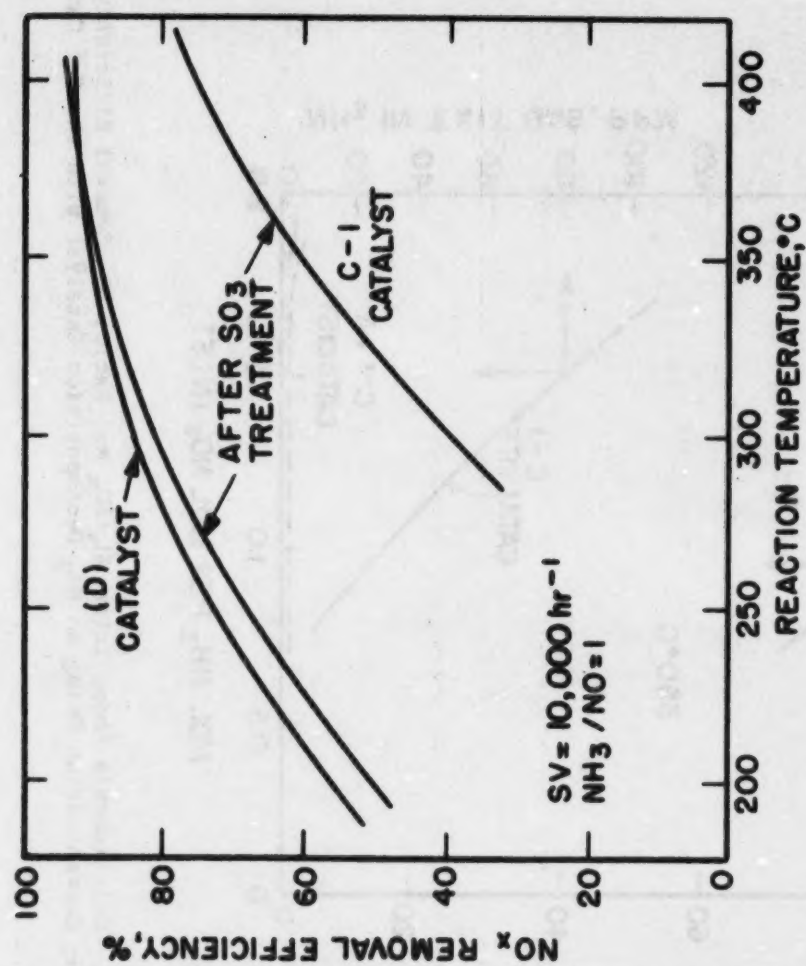


Figure 87. Comparison of NO_x Removal Efficiency with Sumitomo Chemical's SO_x-Resistant D Catalyst and C-1 Catalyst (91).

temperature is given in Figure 88. To avoid deposits of NH_4HSO_4 , either the concentrations of NH_3 and SO_3 must be maintained at lower than indicated values or the temperature must be held above the values designated in Figure 88.

Background of Process Developer

Sumitomo Chemical has constructed several commercial denitrification facilities for oil- and gas-fired FGT. These are included in the following table:

Plant owner	Capacity (Nm^3/hr)	Flue gas source	Completion
Higashi Nihon Methanol	200,000	Gas heating furnace	May 1974
Nihon Ammonia	250,000	Gas heating furnace	March 1975
Sumitomo Chemical	200,000	Gas heating furnace	March 1975
Sumitomo Chemical	100,000	Gas-fired boiler	February 1975
Sumitomo Chemical	200,000	Gas-fired boiler	February 1975
Sumitomo Chemical	250,000	Oil-fired boiler	March 1976
Sumitomo Chemical	300,000	Oil-fired boiler	October 1976

Sumitomo has offices in New York, referred to as Sumitomo Chemical America, Inc., and this should provide the accessibility of their NO_x removal process to the U.S. market.

Published Economic Data

³ The spring 1973 plant cost for the NO_x removal facility treating 200,000 Nm^3/hr at the Higashi Nihon CH_3OH plant with flue gas containing 200 ppm NO_x and an $\text{NH}_3:\text{NO}_x$ mol ratio of 1:1 was \$830,000 (101). This cost is about \$12.6/kW. The corresponding revenue requirement is 1.2 mills/kWh (101). This plant, however, operated with clean gas according to the flowsheet in Figure 89 and does not include an ESP, heat exchanger, and auxiliary heater. The 1976 cost for a plant to treat dirty gas has been reported to be about \$80/kW (5) which includes an ESP. The site location basis was assumed to be Japan.

Raw Material, Energy, and Operation Requirements

For the 200,000 Nm^3/hr treatment facility with flue gas containing 200 ppm NO_x and employing an $\text{NH}_3:\text{NO}_x$ mol ratio of 1:1, the raw material and energy requirements are as follows:

Material	Quantity
NH_3	0.73 short tons/day
Electricity	800 kW

The catalyst consumption is not reported in literature.

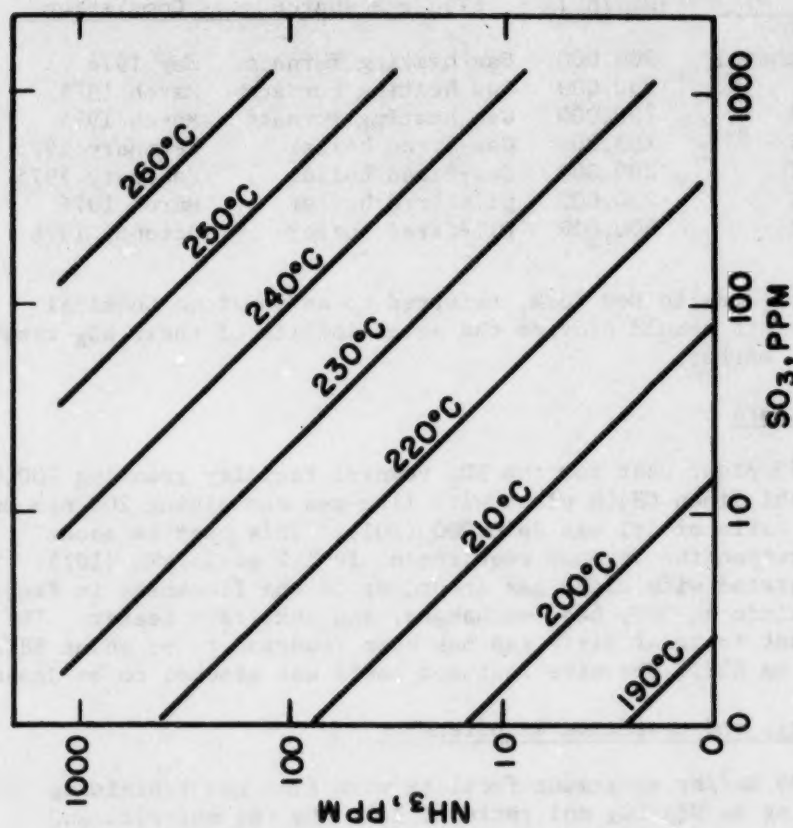


Figure 88. Temperatures Below Which NH_4HSO_4 Forms (101).

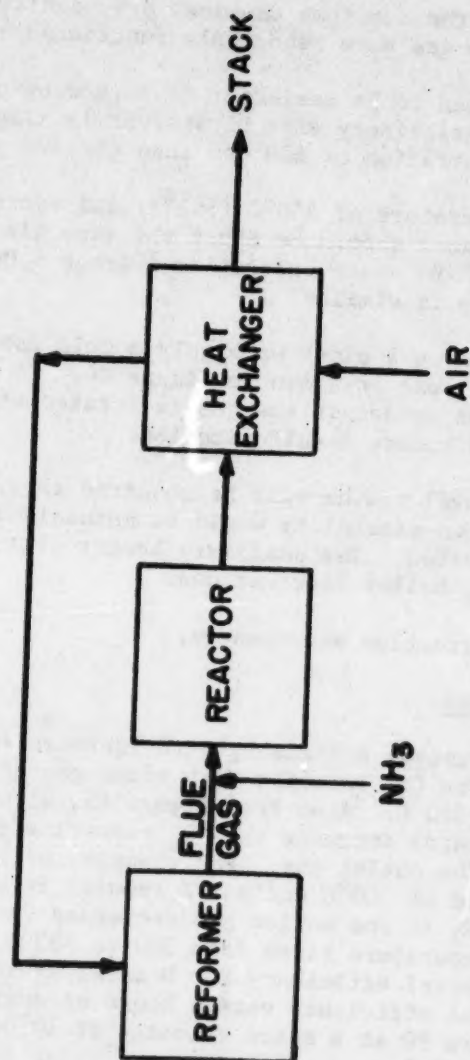


Figure 89. Simplified Flow Diagram of the Flue Gas Treatment Facility at Higashi Nihon Methanol Plant (101).

The electricity needed represents 1.2% of the equiv total power output of the plant. Fuel is not needed at the above plant and fuel requirements for the case described in the flow diagram for dirty gas treatment (Figure 84) are not available. There is no additional manpower required for the 200,000 Nm³/hr capacity plant above.

Technical Considerations

Plant operations using the Sumitomo Chemical dry, denitrification system with oil- and gas-fired flue gas have reportedly functioned smoothly.

The D catalyst is claimed to be resistant to poisoning or deterioration from SO₃. The NO_x removal efficiency with D catalyst is slightly greater with an inlet gas NO_x concentration of 600 ppm than for 100 ppm.

With the reaction temperature of 350°C (662°F) and space velocity of 10,000 hr⁻¹, the reactor vessel should be about the same size as most dry denitrification processes where space velocities average 5,000-10,000 hr⁻¹ and the reaction temperature is similar.

In retrofit application on a plant with only a cold ESP or FGD, the required equipment would be just as shown in Figure 84. If an FGD unit is present, more reheat will be needed if the gas is treated after desulfurization than if it could be treated before desulfurization.

Since several NO_x removal trains will be required to treat the flue gas from a 500-MW plant, turndown capability would be maintained by removal of trains from service as required. The auxiliary heater will aid in controlling reaction temperature during boiler fluctuations.

The materials of construction are unknown.

Environmental Considerations

The increase in NO_x removal efficiency with increase in NH₃:NO_x mol ratio can be seen in Figure 85 for C-1 catalyst with clean gas at a space velocity of 20,000 hr⁻¹ at 300 and 350°C. Also from Figure 85, with the same NH₃:NO_x ratio, increasing temperatures increase the NO_x removal efficiency and decrease the NH₃ concentration in the outlet gas. For example, with NH₃:NO_x = 1:1, 85% NO_x removal is attained at 300°C while 90% removal is obtained at 350°C. At the same conditions, NH₃ in the outlet gas decreases from about 40 ppm to about 10 ppm as the temperature rises from 300 to 350°C. The reaction temperature versus NO_x removal efficiency for D catalyst is displayed in Figure 87. The NO_x removal efficiency versus hours of operation for D catalyst is given in Figure 90 at a space velocity of 10,000 hr⁻¹, 350°C temperature, and NH₃:NO_x = 1:1.

The Sumitomo Chemical denitrification process removes no other pollutants and creates no byproducts. There is no waste to dispose of and, though there is potential for NH₄HSO₄ formation, this occurrence can be avoided as long as operating conditions, given by Figure 88, are satisfied.

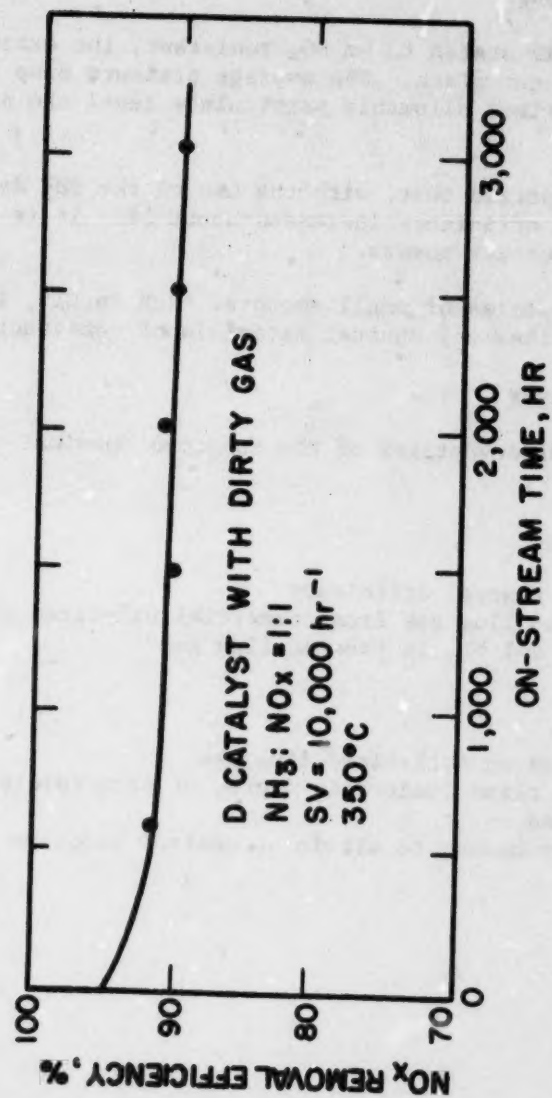


Figure 90. Result of Life Test for Sumitomo Chemical Catalyst (91).

There are no apparent work hazards with this process.

Critical Data Gaps and Poorly Understood Phenomena

The cost, consumption, and life of the base-metal catalyst used by Sumitomo Chemical are not known. The operating cost for denitrification of a dirty gas is unavailable (the cost included earlier was for treatment of a clean gas). Also, fuel and electric requirements are not mentioned for treatment of a gas containing SO_x .

Although D catalyst is stated to be SO_x resistant, the exact maximum, tolerable level of SO_x is not given. The average pressure drop across the reactor system and the maximum allowable particulate level are not released either.

Sumitomo Chemical reported that, with the use of the NH_3 decomposition catalyst, the NO_x removal efficiency increased about 5%. It is uncertain how this NO_x reduction increase occurs.

The effects of gas species of small amounts, such as Cl^- , is not known. Also, it is not known whether any unusual materials of construction are used.

Advantages and Disadvantages

The advantages and disadvantages of the Sumitomo Chemical process are as follows:

Advantages

1. Achieves >90% NO_x removal efficiency
2. Has been applied to flue gas from commercial oil-fired boilers
3. Claims <10 ppm by vol NH_3 in treated flue gas

Disadvantages

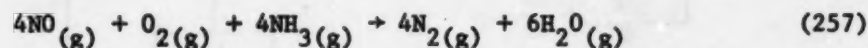
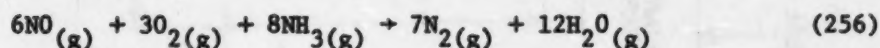
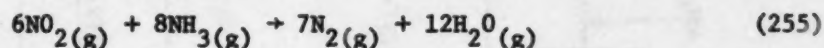
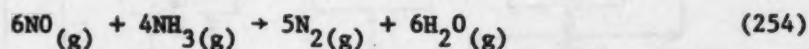
1. Has not been tested on coal-fired flue gas
2. Requires somewhat clean (uncertain degree of particulate removal required) gas feed
3. Requires auxiliary heater to attain or control reaction temperature

SUMITOMO HEAVY INDUSTRIES PROCESS - DRY, SCR (NO_x-SO_x)

Process Description and Principles of Operation (23, 102, 103, 104, 111)

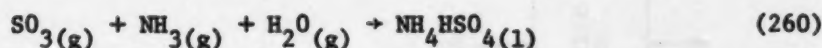
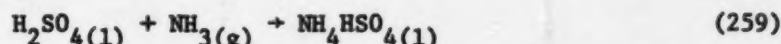
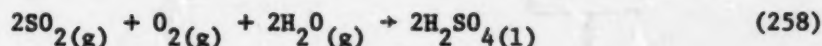
Sumitomo Heavy Industries, Ltd., (SHI) uses an activated C catalyst in their process for simultaneous NO_x-SO_x removal. The NO_x is converted to N₂ by catalytic reduction with NH₃ and SO_x is adsorbed on the catalyst in the form of H₂SO₄ and NH₄HSO₄. This method is very similar to the Takeda Chemical Industries, Ltd., process. The flow diagram for this process is given in Figure 91.

Flue gas, after leaving the air heater and having particulates removed, is heated to reaction temperature by an inline heater. NH₃ is then injected into the flue gas as it enters a moving-bed reactor operating at 200-230°C (392-446°F). In the reactor, the denitrification reactions are stated by SHI to occur as follows:

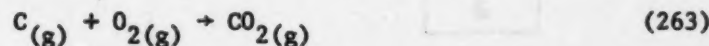
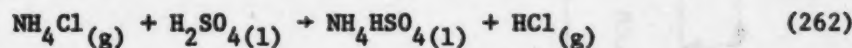


The NO_x is reduced by the NH₃ to harmless N₂ and H₂O which pass through the reactor to the stack with the main flue gas.

The removal of SO_x from the flue gas proceeds by the following equations:



The H₂SO₄ and NH₄HSO₄ are adsorbed on the catalyst. Other minor reactions occurring in the reactor include:



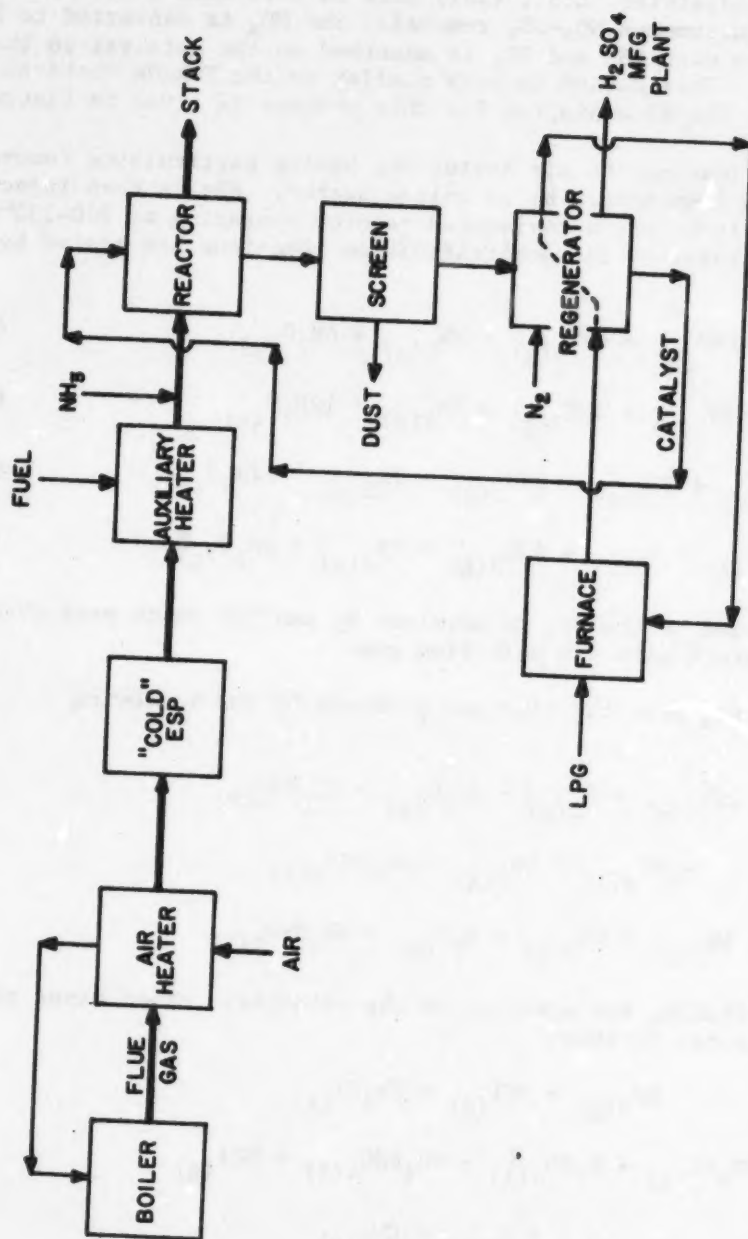


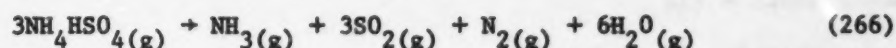
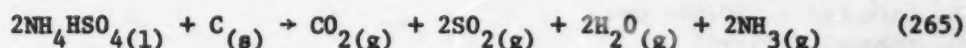
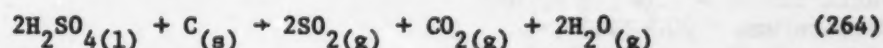
Figure 91. Flow Diagram of Sumitomo Heavy Industries Process.

A small amount of HCl and NH₄Cl formed in reactions (261) and (262) exits in the treated flue gas. Reaction (261) represents a slight NH₃ consumption which must be compensated by an additional amount of NH₃ being injected into the flue gas. Reaction (263) represents a catalyst loss.

The reactor temperature ranges from 200-230°C (392-446°F). Other normal operating conditions include a space velocity of 1000 hr⁻¹ and an NH₃:NO_x mol ratio range of 2:1-2.5:1. The maximum particulate loading which has been tested is 0.2 g/Nm³ (0.086 gr/sft³).

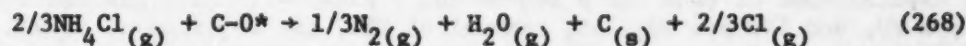
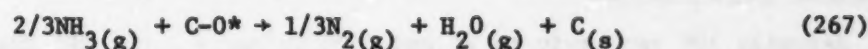
The treated flue gas passes through the reactor and is vented out the stack.

The catalyst is continuously moving downward in the reactor with the flue gas fed in a crossflow pattern to the catalyst bed. The catalyst exiting the bottom of the reactor is screened in the presence of an inert gas, N₂, to remove deposits before entering the regenerator. A temperature of about 350°C (662°F) is maintained by the passage of hot gas from a furnace burning LPG through a heat exchanger within the regenerator. The main reactions taking place in the regenerator are as follows:



The inert gas exiting the regenerator contains 10-15% SO₂ and is suitable for feed gas for manufacturing H₂SO₄. The hot gas used to maintain the regenerator temperature is recycled back to the LPG-burning furnace. Catalyst is lost as a result of reactions (264) and (265) occurring and this loss increases in direct proportion to the SO_x content of the incoming flue gas. Therefore, this process is not recommended for coal-fired FGT where SO₂ levels exceed 600 ppm. (See Raw Material, Energy, and Operation Requirements.)

Additional reactions proceeding in the regenerator include:



(*C-O represents O₂ chemically bonded with or adsorbed on the catalyst).

This system may remove 85-90% NO_x and 95% SO_x from the flue gas.

Status of Development

SHI began developing a process and testing of catalysts using laboratory facilities in 1973. In 1974, bench-scale tests with a capacity of 150 Nm³/hr (0.05 MW equiv) started and continued through mid-1975. This operation was performed on flue gas from an oil-fired boiler and with a fixed-bed reactor. SHI converted to a moving-bed reactor by drawing from 3 yr of experience at the 175,000 Nm³/hr capacity oil-fired FGD plant of Kansai Electric Power Company. SHI began tests in April 1976 with a 2000 Nm³/hr (0.7 MW equiv) pilot plant treating flue gas from a steel mill sintering plant. Upon completion of these tests in August 1976, the pilot plant was enlarged to 10,000 Nm³/hr (3.3 MW equiv) capacity and operated from October 1976 through March 1977. Typical conditions for the operation of these plants are as follows:

Inlet flue gas composition

NO_x = 150-200 ppm
SO₂ = 350-480 ppm
O₂ = 12-15%
H₂O = 10-12%
Particulates = 120-150 mg/Nm³
Temperature = 200-230°C
Space velocity = 1000-1700 hr⁻¹
NH₃ injected = 350-500 ppm
NO_x removal = 85-90%
SO₂ removal = 95%

Background of Process Developer

Since 1965, SHI investigated SO₂ removal from flue gas from oil-fired boilers. The FGD process of SHI has been in commercial use since 1972. The SO_x-NO_x simultaneous removal process is still under development for applications with flue gas containing <600 ppm SO₂ (see Raw Material, Energy, and Operation Requirements). An NO_x-only process is being developed for coal-fired FGT (see next process description). SHI has offices in New York which would make the process more accessible in the U.S.

Published Economic Data

Assuming 300 yen equiv to \$1 and 3000 Nm³/hr = 1 MW, SHI claims (23) a 1977 capital cost of \$23M for a 500-MW equiv plant with flue gas containing 600 ppm NO_x and 500 ppm SO₂, SO_x removal of 95%, and NO_x removal of 90%. Included as part of the capital cost is \$6.4M for the catalyst which cost about \$4170/metric ton. This capital cost equals \$46/kW. The operating cost is equal to 5.9 mills/kWh (based on 233-MW-equiv plant with flue gas containing 200 ppm NO_x and 500 ppm SO₂ and 1976 costs) (102). These figures are assumed to be based on Japanese location and to include both the removal system and H₂SO₄ manufacturing plant though not stated specifically by SHI. (1973 figures on FGD unit only indicated the H₂SO₄ manufacturing unit to be 10% of the investment.)

Raw Material, Energy, and Operation Requirements

The estimated NH_3 usage rate is 55 short tons/day for a 500-MW-equiv plant with 600 ppm NO_x and 500 ppm SO_x in the inlet gas, 95% SO_x removal, and 90% NO_x removal.

There is a substantial C loss, as noted in reactions (263), (264), and (265). For the same 500-MW equiv-basis, as above, an initial catalyst charge of 1716 short tons is needed. The catalyst makeup rate required is 3300 short tons/yr. The rate of C consumption increases in direct proportion to the increase in SO_x content of the flue gas, so that, C loss would be correspondingly large for a 500-MW, coal-fired plant with flue gas containing 2400 ppm SO_2 . SHI states that an SO_2 level of 600 ppm in the flue gas is the maximum level allowed for economical operation.

The energy consumption values on the same basis as the above NH_3 usage rate are as follows:

Utility	Quantity
Electricity	3100 kW
Steam	26 short tons/day
Cooling water	5 m ³ /hr
LPG	25 short tons/day

The electrical requirement represents 0.95% of the total equivalent power of the plant.

The operating manpower requirement for a 500-MW equiv-FGT system is estimated at two man/shift.

Technical Considerations

This simultaneous SO_x - NO_x removal system is slightly more complex than most dry NO_x removal-only systems since it possesses a moving-catalyst bed and a regeneration unit. It is similar to the Kurabo process in this respect. SHI's process also includes an H_2SO_4 manufacturing unit for the treatment of the SO_2 -containing regeneration gas.

Little information has been released on the sensitivity of the process to inlet gas composition. It is known that the activated C loss is increased with higher SO_2 concentrations in the flue gas.

The absorber vessel will be considerably larger for this system than most competitive processes. Though the reaction temperature (200-300°C) is considerably less than most SCR methods (400°C), the space velocity (1000 hr⁻¹) is significantly lower than the average of other processes (5000-10,000 hr⁻¹), thus, requiring a larger reaction vessel.

This simultaneous SO_x - NO_x removal process may be applicable for retrofit application for a coal-fired plant with an existing FGD facility. Since the SO_2 level would be lowered to <600 ppm in the gas after an FGD unit, the activated C consumption loss would not be as great as previously mentioned. Reheat would be required to obtain the required reaction temperature (200-300°C).

For a plant with a cold ESP and no existing FGD unit, an inline heater for a small amount of reheat due to low reaction temperature is needed. This is in comparison to the need of a hot ESP and possibly a heat exchanger for other dry processes. The area required may be larger than other processes because of the larger reaction vessels and H_2SO_4 manufacturing unit.

Since several FGT trains are required, adequate turndown capacity should be maintained by simply removing a train from use. Also, the inline heater should provide some reactor temperature control during boiler load variation.

The material of construction is primarily carbon steel but there are some stainless steel portions.

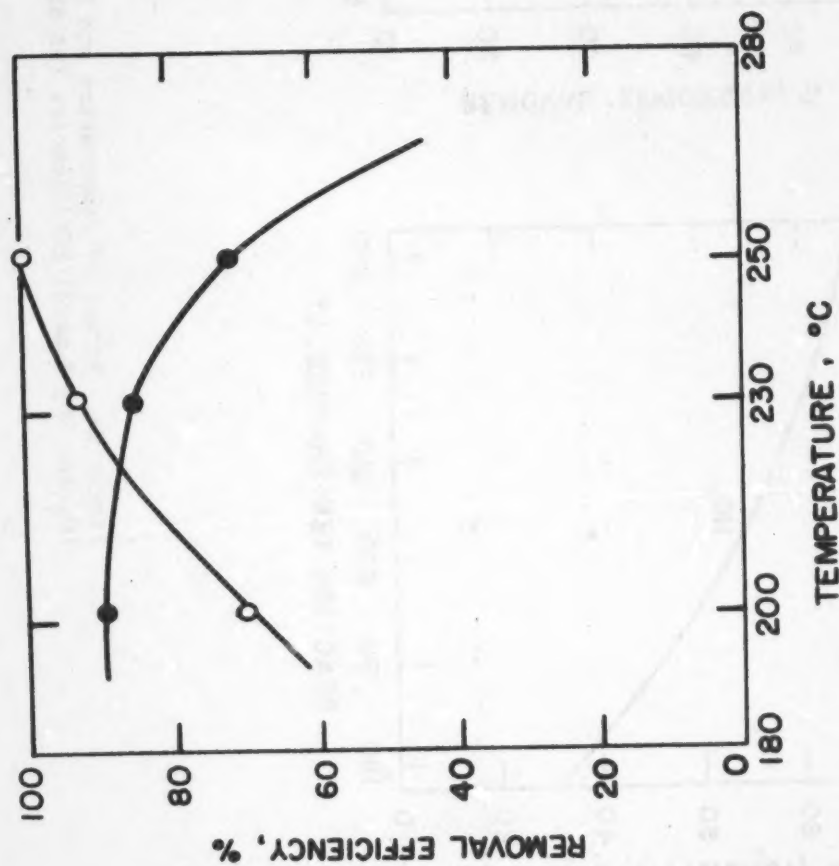
The SO_2 -rich gas exiting the regenerator is used to manufacture 98% concentrated H_2SO_4 , which is considered to be of marketable quality.

Environmental Considerations

With flue gas containing 300 ppm NO and 600 ppm SO_x , a space velocity of 1000 hr^{-1} , and a 2:1 mol ratio of NH_3 : NO_x , the NO_x removal efficiency increases from 70% to >95% as the reaction temperature increases from 200 to 250°C (392-482°F). The SO_x removal efficiency decreases from 90% to about 70% as the temperature rises from 200 to 250°C. The NO_x and SO_x removal range from 80-90% each at 220°C (428°F). These data are shown in Figure 92. Sensitivity of NO_x and SO_2 removal efficiencies to temperature, space velocity, and NH_3 injection is given in Figures 93 and 94. These results were obtained from the pilot plant operating at 2000 Nm^3/gr capacity at typical conditions previously described in the Status of Development section. Again it is noted that as the temperature increases, NO_x removal increases while SO_2 removal is reduced (Figure 93). As the space velocity rises from 1000 to 1700 hr^{-1} , NO_x removal decreases as expected but still remains above 80% (Figure 93). Figure 94 shows that the NO_x removal efficiency increases as the inlet NH_3 concentration increases. The NH_3 exiting the system is also displayed.

Along with NO_x , this process simultaneously removes SO_x from the flue gas. A small amount of particulate matter is also extracted but the maximum particulate loading which has been tested is 0.2 g/Nm^3 (0.085 gr/sft^3); therefore, particulate removal is considered necessary for applications of this process to coal-fired boiler flue gas.

There should be no major waste-disposal problems; however, the dust screened from the catalyst bed would require handling. There is potential for secondary pollution with NH_4Cl and excess NH_3 exiting the stack.



CONDITIONS:

- NO_x CONTENT: 300 PPM
- SO_x CONTENT: 600 PPM
- SPACE VELOCITY: 1000 HR⁻¹
- NH₃ / NO_x RATIO : 2:1

Figure 92. Effect of Temperature on NO_x and SO₂ Removal Efficiencies with SHI Carbon-Based Catalyst (102).

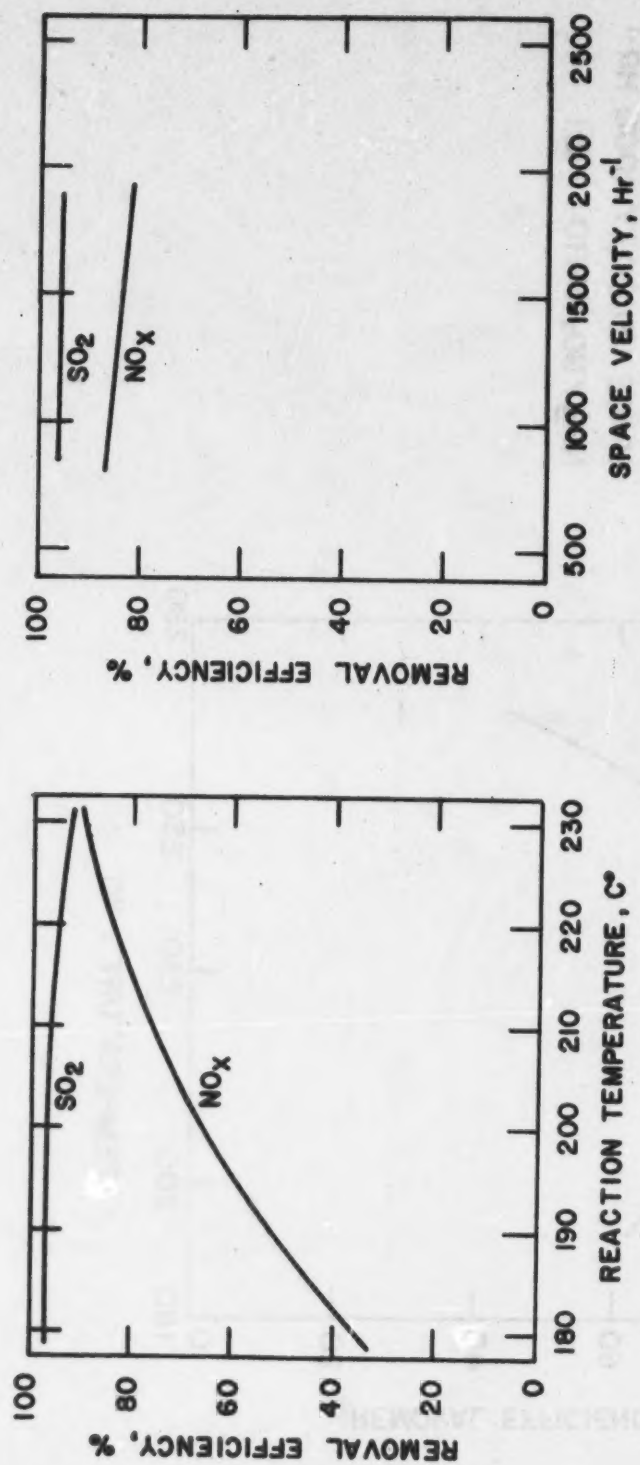


Figure 93. Effect of Temperature and Space Velocity on NO_x and SO₂ Removal Efficiencies for SHI Process (103).

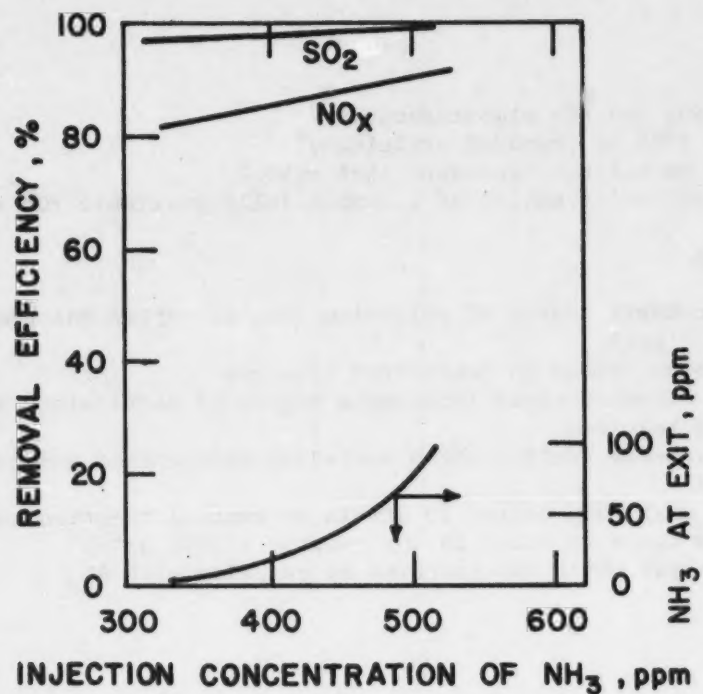


Figure 94. Effect of NH_3 Injection Rate on NO_x and SO_2 Removal Efficiencies for SHI Process (103).

There are no apparent work hazards.

Critical Data Gaps and Poorly Understood Phenomena

A critical data gap is the time required for the C-based catalyst to complete a cycle (reactor → regenerator → reactor). It will vary with the SO₂ concentration and particulate level of the flue gas.

Advantages and Disadvantages

A listing of the major advantages and disadvantages of the SHI process is as follows:

Advantages

1. Removes NO_x and SO₂ simultaneously
2. Achieves >95% SO₂ removal efficiency
3. Produces marketable byproduct (98% H₂SO₄)
4. Is a slight modification of a commercially available FGD system

Disadvantages

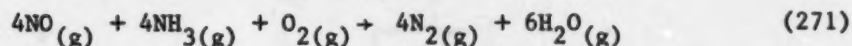
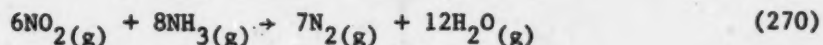
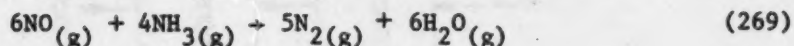
1. Forms secondary source of pollution (NH₃ in outlet gas probably exceeds 10 ppm)
2. Has not been tested on coal-fired flue gas
3. Requires somewhat clean (uncertain degree of particulate removal required) gas feed
4. Uses moving-bed reactor which increases maintenance and catalyst attrition
5. Requires auxiliary heater to attain or control reaction temperatures
6. Has a low space velocity in the reactor (<5000 hr⁻¹)
7. Uses catalyst which deteriorates by reaction with SO₂

SUMITOMO HEAVY INDUSTRIES PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (102, 111)

In addition to a simultaneous SO_x-NO_x removal process, Sumitomo Heavy Industries, Ltd., (SHI) is developing an SCR method of NO_x removal only. The NO_x is reduced to N₂ by reaction with NH₃ in the presence of a metal-oxide catalyst. Figure 95 shows a simplified flow diagram of the process.

Having passed through the air heater and through some type of particulate removal (cold ESP for example), the flue gas is heated by an inline heater to the reaction temperature of 270-370°C (518-698°F). NH₃ is injected into the flue gas before it enters the reactor. In the reactor NO_x is reduced to harmless N₂ by NH₃ aided by a metal-oxide catalyst as follows:



The reactor is a moving-bed type with the flue gas flowing in a cross-flow pattern to the catalyst flow. The catalyst moves downward through the reactor and after exiting the reactor, passes over screens for ash removal before being conveyed back to the top of the reactor. The treated flue gas exits the reactor and passes to the stack or an FGD unit.

The average NH₃:NO_x mol ratio is 1:1 and the space velocity is usually >5000 hr⁻¹ depending upon temperature. With the reaction temperature of 270-330°C (518-626°F) the NO_x removal efficiency is <85%. The NO_x removal efficiency is >90% with reaction temperature above 350°C (662°F).

Status of Development

Since late 1975, SHI has been testing an SCR process for the removal of NO_x using a metal-oxide catalyst. A bench unit of 500 Nm³/hr (0.2 MW equiv) capacity with a moving-bed reactor was initially used for development and has been enlarged to a capacity of 1500 Nm³/hr (0.5 MW equiv) for further development. A steel mill sintering plant is the flue gas source. The catalyst life has exceeded 5600 operating hr in bench unit tests.

Background of Process Developer

SHI has been involved in research and development of SO₂ removal from oil-fired flue gas since 1965. The FGD process has been in commercial use at a 175,000 Nm³/hr capacity plant since 1972. The NO_x removal process with the metal-oxide catalyst is still in the early stages of development.

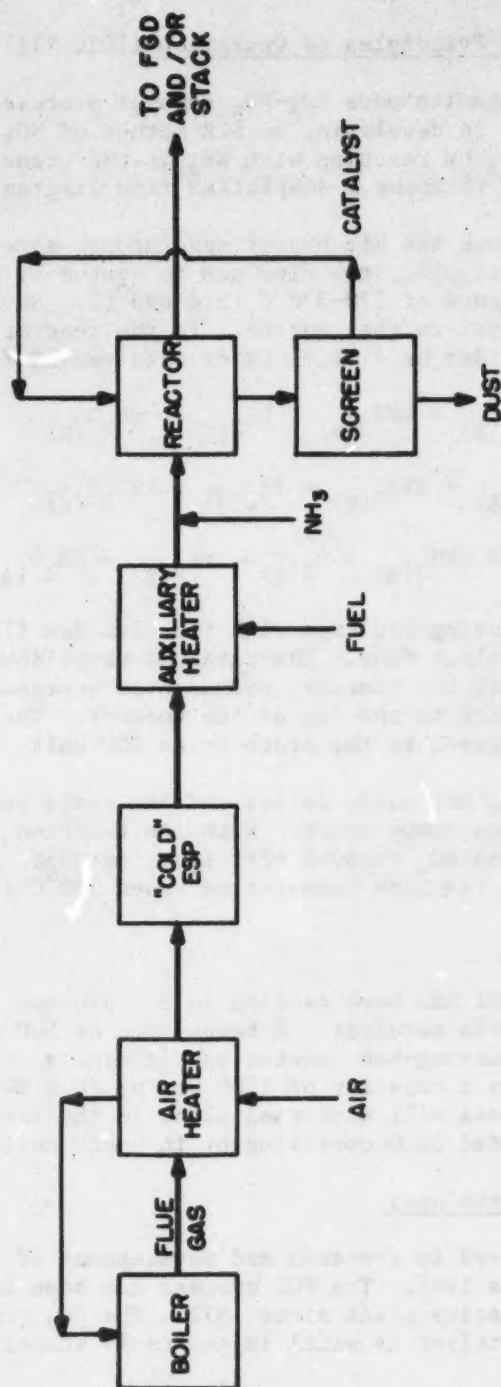


Figure 95. Flow Diagram of Sumitomo Heavy Industries Process.

The SHI process should be readily available in the U.S. since there are SHI offices in New York.

Published Economic Data

The estimated capital investment (111) for a 500-MW equiv-plant is \$14.8M, which is about \$30/kW. The revenue requirement is 2.3 mills/kWh with inlet gas containing 600 ppm NO_x (111). These are assumed to be based on 1976 costs and a Japanese location.

Raw Material, Energy, and Operation Requirements

It is estimated that the required NH_3 for a 500-MW plant with flue gas containing 600 ppm NO_x is 20 tons/day.

The fuel and energy requirements (electricity and steam) are not given. Operating, maintenance, and technical support requirements are not available either. These however should be very similar to other dry, SCR methods for removing NO_x only.

Technical Considerations

This process is simple as is typical of other SCR processes. The major control factors will be NH_3 flow rate and reaction temperature, both of which should be capable of automatic control.

In Figure 96 the NO_x removal is shown at various concentrations of SO_2 in the flue gas. For example, at 300°C (572°F) the % NO_x removal was 80% at a 0 ppm SO_2 concentration and 85% at a 600 ppm SO_2 concentration.

Since the space velocity of $5,000 \text{ hr}^{-1}$ is about average in comparison to other processes ($5,000$ – $10,000 \text{ hr}^{-1}$) and the reaction temperature of 300°C (572°F) is lower compared to the 400°C (752°F) of most processes, the reaction vessel size that is required may be slightly smaller than for competitive processes.

For retrofit application of this SHI process on a plant with an existing FGD unit, more reheat is required to reach reaction temperature (270 – 370°C) if the flue gas has to be treated after the FGD unit than if NO_x removal is applied before the FGD system. If a plant has only a cold ESP, the reheat is the same as required above for treating gas before the FGD unit. In either case, less reheat is needed for the SHI process if operated at about 270 – 330°C than most dry processes with reaction temperatures of 350 – 400°C .

Since several trains would be needed for treatment of flue gas from a 500-MW capacity plant, the main turndown capability is in the removal of trains from service as necessary. An inline heater would provide reactor temperature control during boiler load variations.

There is no information on materials of construction. Also, there are no byproducts created by this process.

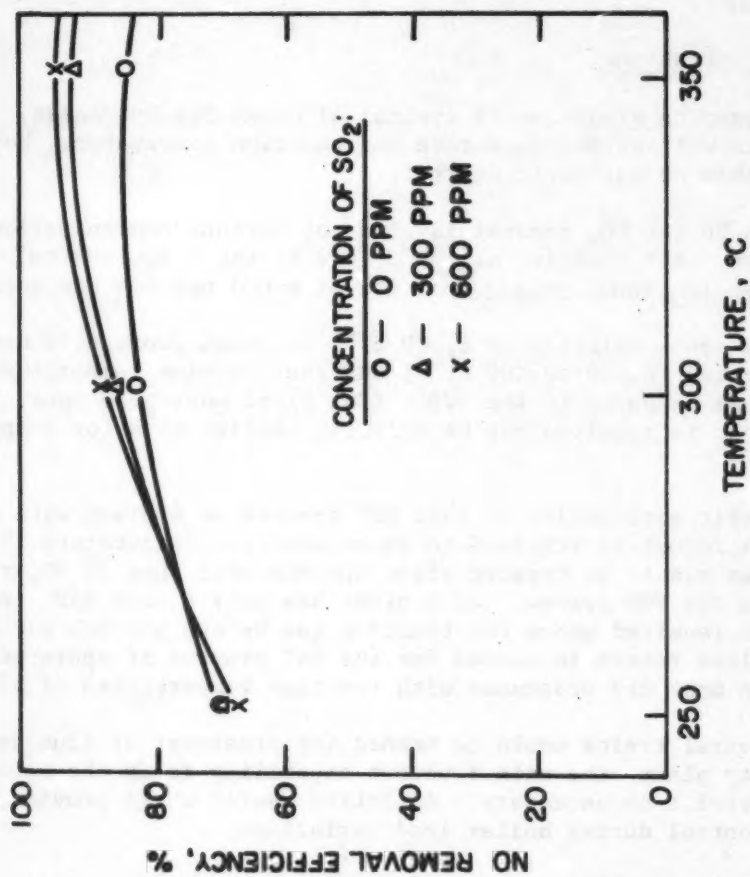


Figure 96. Effect of Temperature and SO₂ on NO Removal Efficiency with SHI Metal-Oxide Catalyst (102).

Environmental Considerations

The available data on sensitivity of NO_x removal efficiency to various parameters is shown in Figure 96. The NO_x removal efficiency increased from 70 to >85% when the temperature of reaction was increased from 250°C (482°F) to 300°C (572°F) with flue gas containing 150 ppm NO_x and 300-600 ppm SO_x . With an increase in reaction temperature of 300°C to 350°C (662°F) the efficiency increased only a few percent. No information is available on effects of removal efficiency by varying $\text{NH}_3:\text{NO}_x$ ratio, higher flue gas SO_2 concentrations, space velocity, etc.

The SHI process is claimed to remove some ash by use of a moving catalyst bed which passes the catalyst from the reactor over a set of screens and then returns the catalyst to the reactor. A possible disadvantage of the moving bed and screens may be the early deterioration of the catalyst. No mention is made by SHI of the physical strength of the metal-oxide catalyst. No pollutants other than NO_x are removed to any extent from the flue gas by this process.

There are no major wastes for disposal with this process; the dust separated during the catalyst screening step will require handling. There is the potential for excess NH_3 to exit at the stack and though the formation of NH_4HSO_4 is more likely at lower reaction temperatures, SHI states that no reaction of NH_3 with SO_x occurs at $270\text{--}330^\circ\text{C}$ ($518\text{--}626^\circ\text{F}$). There are no apparent work hazards.

Critical Data Gaps and Poorly Understood Phenomena

Included in the data gaps are the effects on the NO_x removal efficiency by factors such as $\text{NH}_3:\text{NO}_x$ mol ratios and SO_2 concentrations in the inlet gas >600 ppm. The NO_x removal as a function of space velocity and the effects of Cl^- in flue gas from a coal-fired boiler are unknown.

The pressure drop across the reactor, the maximum tolerable particulate level, the expected catalyst life, and catalyst cost are not available. It is not known whether there is a problem with excess NH_3 exiting at the stack nor is formation of NH_4HSO_4 in the system mentioned.

In considering requirements for this process, the fuel, electricity, and steam consumption have not been given yet by SHI. The exact NH_3 usage has not been stated by SHI though it can be estimated at 20 short tons/day for a 500-MW capacity-plant with flue gas containing 600 ppm NO_x and based on an $\text{NH}_3:\text{NO}_x$ ratio of 1:1.

There is also a lack of information on maintenance and technical support requirements, and the required materials of construction.

Advantages and Disadvantages

The advantages and disadvantages of the SHI dry, SCR method of removing NO_x are as follows.

Advantages

1. Achieves >90% NO_x removal efficiency

Disadvantages

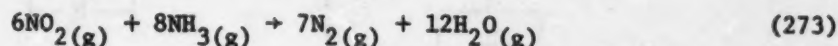
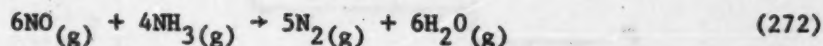
1. Has not been tested on coal-fired flue gas
2. Requires somewhat clean (degree of particulate removal required is uncertain) gas feed
3. Uses moving-bed reactor which increases maintenance and catalyst attrition
4. Requires auxiliary heater to attain or control reaction temperature

TAKEDA PROCESS - DRY, SCR (NO_x - SO_x)

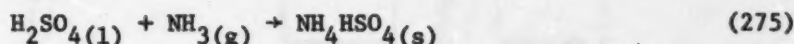
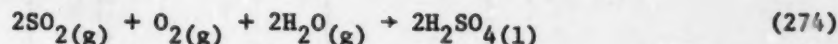
Process Description and Principles of Operation (5, 48)

Takeda Chemical Industries, Ltd., is offering a simultaneous NO_x - SO_2 removal process. NO_x removal is accomplished by a SCR of NO_x with NH_3 in the presence of an activated C catalyst. SO_2 is adsorbed by the catalyst in the form of H_2SO_4 and NH_4HSO_4 .

The optimum temperature range for 90% NO_x removal and greater than or equal to 80% SO_2 removal in the NO_x - SO_2 removal vessel is 210-250°C (410-482°F). It is therefore assumed that for a coal-fired power plant, the flue gas would pass from the air preheater through a cold ESP and then be heated by heat exchanger and heater to reaction temperature (see Figure 97 or 98). Between the heater and reactor, NH_3 is injected into the flue gas stream. In the reactor NO_x is reduced to N_2 according to the following equations:



While the NO_x is reduced to N_2 , the SO_2 is being adsorbed on the C catalyst in the form of H_2SO_4 and NH_4HSO_4 . These are formed as follows:



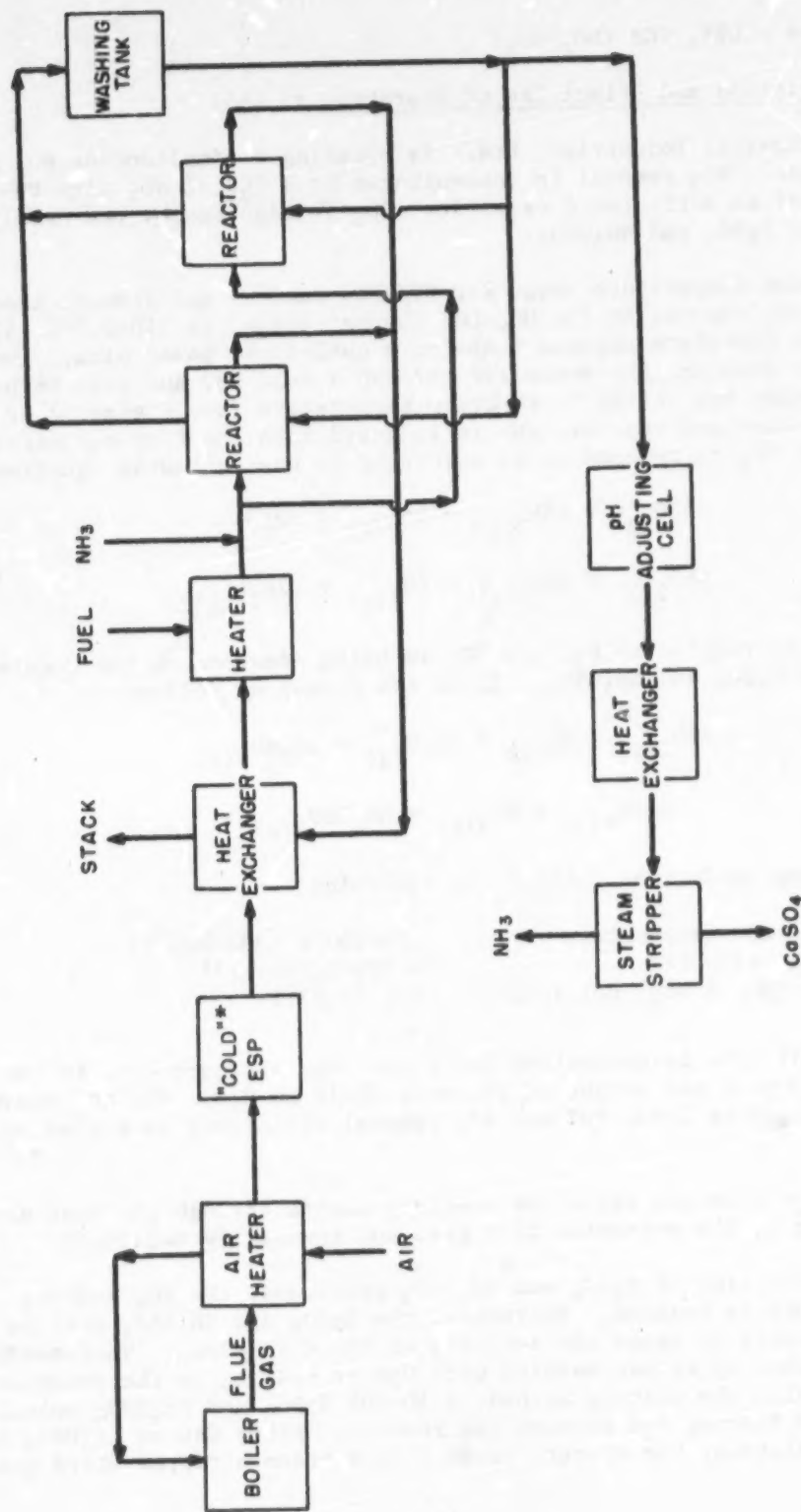
Typical operating conditions include the following:

Reaction temperature	200-250°C (392-482°F)
Space velocity	1,000-3,000 hr^{-1}
NH_3 :(NO_x + SO_2) mol ratio	(0.7-1.2):1

The catalyst life is guaranteed for 1 yr. The pressure drop in the catalyst layer over a bed height of 50 cm is 30-70 mm H_2O . The NO_x removal efficiency averages at least 90% and SO_x removal efficiency is a minimum of 80%.

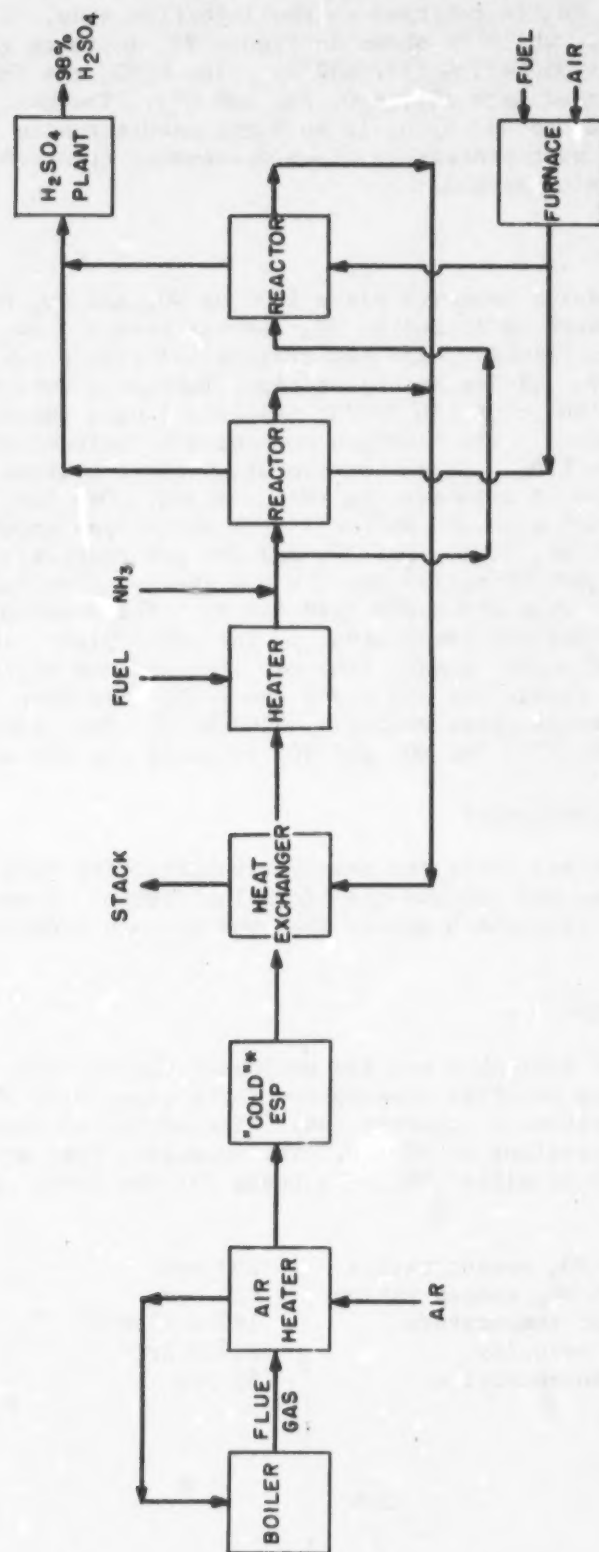
The treated flue gas exits the reactor, passes through the heat exchanger to transfer heat to the untreated flue gas, and then exits the stack.

As the adsorption of H_2SO_4 and NH_4HSO_4 continues, the NO_x and SO_2 removal efficiency is reduced. Therefore, the H_2SO_4 and NH_4HSO_4 must be removed periodically to renew the activity of the C catalyst. This removal may be accomplished by either washing with H_2O or heating in the presence of an inert gas. With the washing method, a 10-20% H_2SO_4 and NH_4HSO_4 solution is obtained from forcing H_2O through the reactor. After CaO or $\text{Ca}(\text{OH})_2$ is added to this solution, the mixture is sent to a steam stripper where gaseous



* ASSUMED NECESSARY FOR COAL-FIRED POWER PLANT OPERATION

Figure 97. Flow Diagram of Takeda Chemical Industries, Ltd., Process (Regeneration by Washing).



* ASSUMED NECESSARY FOR COAL-FIRED POWER PLANT OPERATION

Figure 98. Flow Diagram of Takeda Chemical Industries, Ltd., Process (Regeneration by Heating).

NH₃ is taken off the overhead and CaSO₄ is recovered as the stripper bottoms (see Figure 97). The NH₃ is recycled to the injection step. With the heating method of regenerating, which is shown in Figure 98, an inert gas is passed through the reactor at 350-450°C (662-842°F). The H₂SO₄ and NH₄HSO₄ on the C catalyst are decomposed into SO₂, H₂O, N₂, and CO₂. The gas, composed of 5-15% SO₂, is converted to 98% H₂SO₄ in an H₂SO₄ manufacturing plant. This heating method is the most preferable since wastewater treatment would be required with the washing method.

Status of Development

Takeda has been doing research since 1968 on NO_x and SO_x removal. Experimental studies were performed on NO_x removal versus % O₂, % H₂O in flue gas, space velocity, and temperature and also pressure drop versus linear velocity. (Refer to the section, Technical Considerations.) Also, a bench-scale plant with 100 Nm³/hr capacity from a thermal power station has been operated. The flue gas composition included 60-130 ppm NO_x, 50-150 ppm SO_x, and 6-7% O₂. There are two pilot-plant systems in operation with the heating method of regenerating the catalyst. One has flue gas from a sintering furnace with a 10,000 Nm³/hr (33 MW equiv) gas capacity. The inlet flue gas NO_x and SO_x levels are 200 and 300 ppm respectively. The particulate level is 100-200 mg/Nm³ and the average space velocity, 1100 hr⁻¹. The temperature ranges from 210-230°C (410-446°F). The minimum NO_x and SO_x removal levels are 80 and 90% respectively. The other plant with a capacity of 4500 Nm³/hr (1.5 MW equiv) treats flue gas from a glass-melting furnace. The NO_x and SO_x inlet levels are about 300 ppm each. The dust level is 1-5 mg/Nm³ and the average space velocity, 1300 hr⁻¹. The temperature ranges from 200-250°C (392-482°F). The NO_x and SO₂ removals are 90% each.

Background of Process Developer

Takeda is the process owner and catalyst supplier for this simultaneous NO_x-SO₂ removal process and retains the licensing rights. There is an office of Takeda in New York City which should make the process accessible in the U.S.

Published Economic Data

The economic data available are the estimated capital cost and operating cost of utility and raw material consumption for a plant with 100,000 Nm³/hr (33.3 MW equiv) gas treatment capacity (48). The estimated capital cost is about \$3M which is equivalent to \$90/kW. The operating cost equals \$21.80/hr and is equivalent to 0.65 mills/kWh. The basis for the above costs includes the following:

Inlet NO _x concentration	200 ppm
Outlet NO _x concentration	<20 ppm
Exhaust temperature	180°C (356°F)
Space velocity	2,000 hr ⁻¹
SO _x concentration	50 ppm

These costs do not include the system for catalyst regeneration. The cost of the activated C is approximately \$4170/metric ton and about 60 tons of C catalyst is initially required. It is also assumed that 1976 costs and a site in Japan are basis for the above economics.

Raw Material, Energy, and Operation Requirements

As in the economic data section, the following raw materials and energy requirements are for a 100,000 Nm³/hr gas capacity treatment facility. The basis is the same as mentioned above and only includes the operations involved in NO_x removal and do not include the catalyst regeneration facilities. The requirements are as follows:

Electricity	230 kW
Fuel oil	3.09 short tons/day
NH ₃	0.42 short ton/day

The electricity required for the NO_x removal portion represents 0.7% of the total power equivalent of the plant.

Technical Considerations

Takeda's system is fairly simple compared to wet NO_x removal systems. The regeneration section would make this slightly more complex than some of the other dry NO_x-only removal processes.

The information on removal sensitivity to inlet gas composition is provided by experimental data as shown in Figures 99-102. The gas used contained 300 ppm NO_x and 50 ppm SO₂ and 300 ppm NH₃. In Figure 99 the NO_x removal increased from 45 to 95% as the O₂ increased from 0 to 5%. The NO_x removal decreased from 95 to 90% as the H₂O increased from 5 to 10%. Also, the frequency of regeneration required is dependent upon the concentration of SO_x in the flue gas. It is stated that with an inlet concentration of 150 ppm SO_x, the regeneration is required every few days. For a flue gas from a coal-fired boiler with 2400 ppm SO_x, regeneration would be required approximately every 15 hr. Though the heating method is the most preferable regeneration method, if the washing method were used, H₂O equivalent to five times the catalyst in weight would be required for each period of regeneration.

In Figure 100 the pressure drop data indicate an increase in pressure loss from 35 to 200 mm H₂O when linear gas velocity increases from 0.15 to 0.5 m/sec. This may be a greater pressure loss than most of the other dry systems. Since the space velocity is rather low in comparison to most of the dry processes, the reactor vessels would be about the same to slightly larger. Also, more vessels would be required if the washing step is required. However, with the low reaction temperature, a cold ESP and smaller heaters and heat exchanger are satisfactory.

This process would be suitable for retrofit applicability on a plant with or without FGD equipment. If an FGD process is already present, this system could be placed after the FGD unit and the frequency of regeneration in the Takeda process would be greatly reduced. More reheat would be required

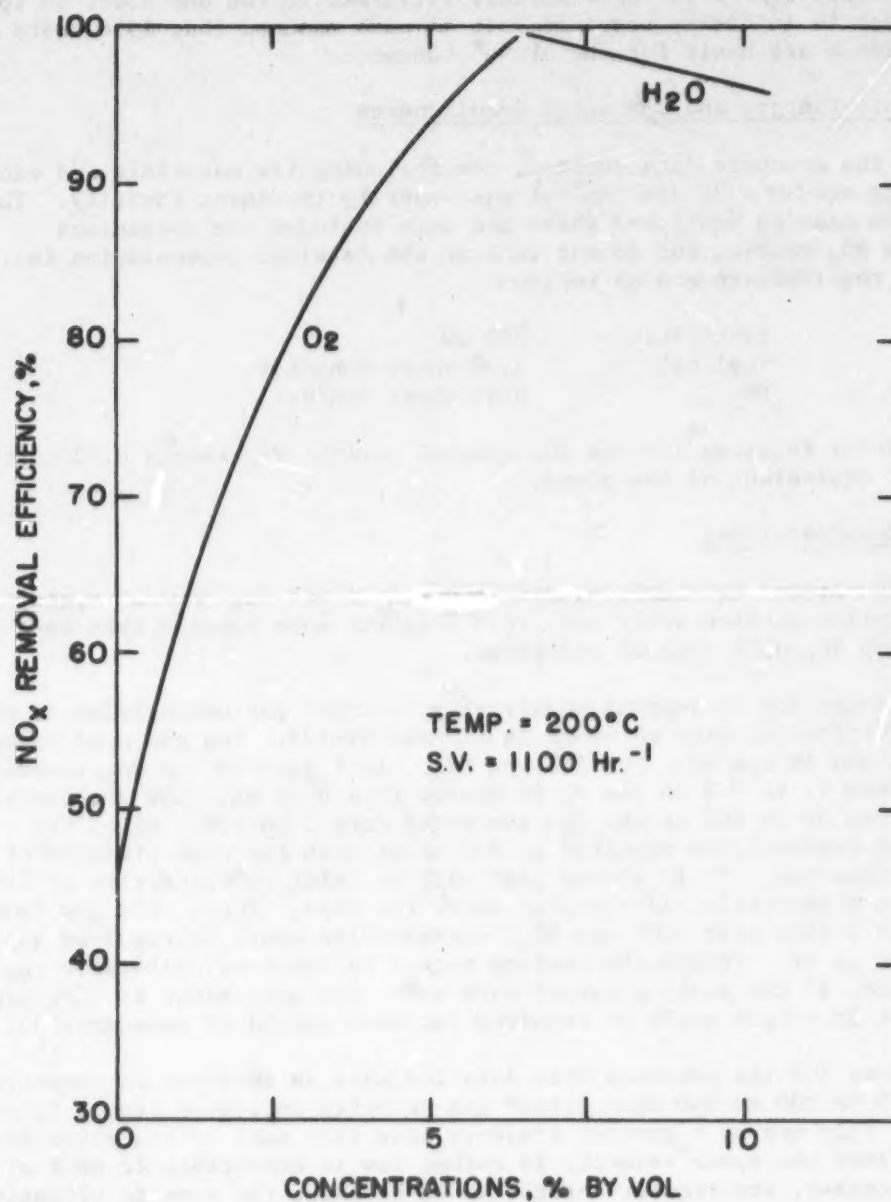


Figure 99. Relationship of O₂ and H₂O Concentration in Flue Gas to NO_x Removal Efficiency for Takeda Process (48).

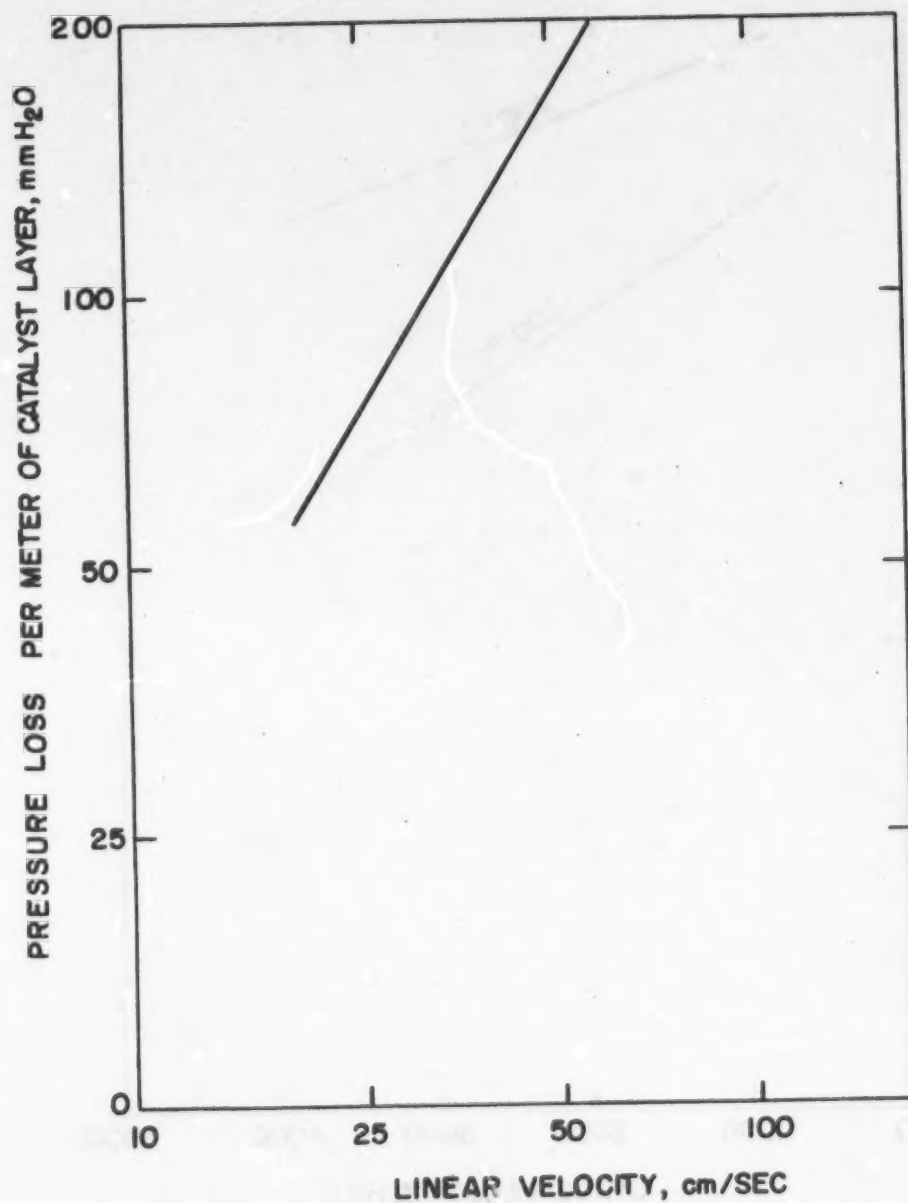


Figure 100. Relationship of Linear Velocity and Pressure Drop for Takeda Process (48).

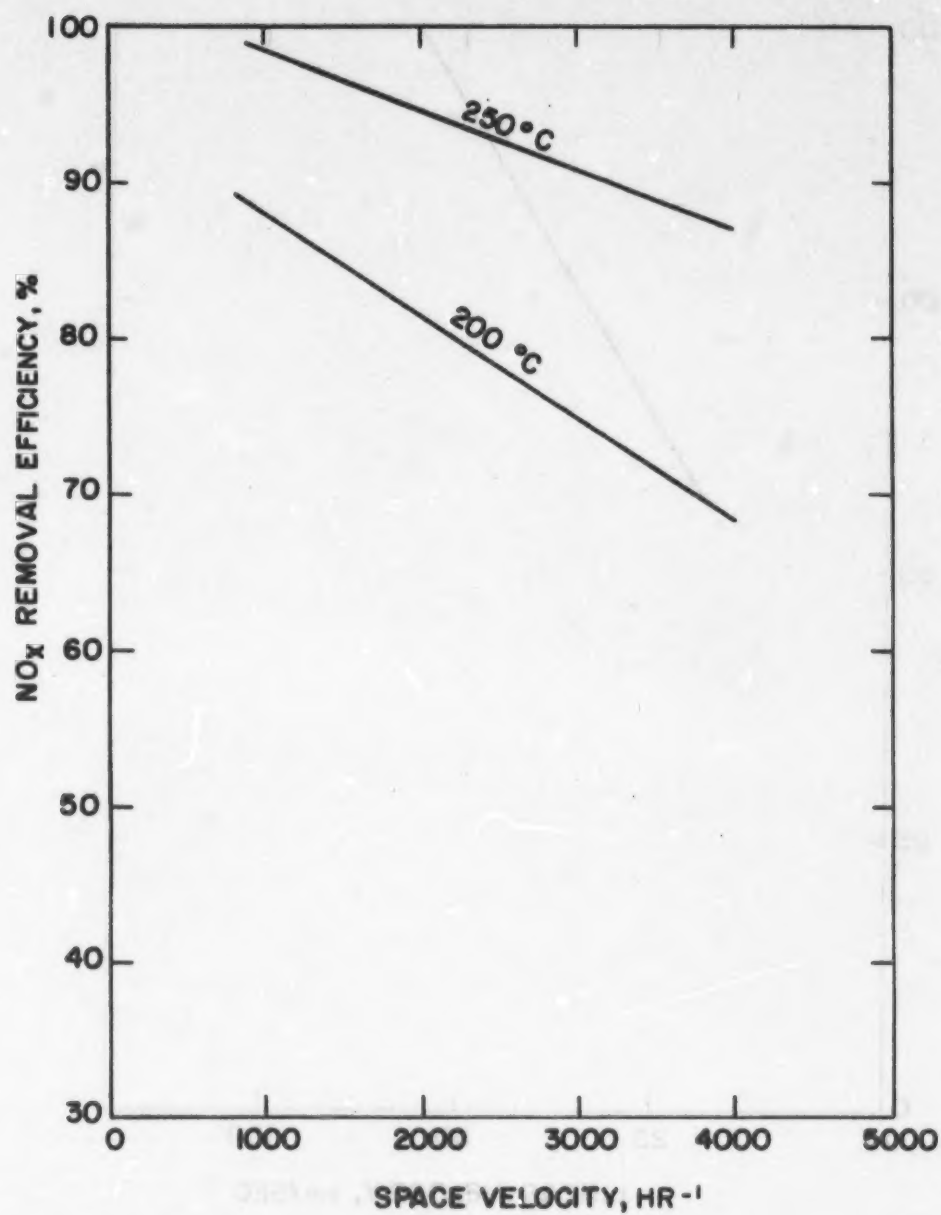


Figure 101. Relationship of Space Velocity and NO_x Removal Efficiency for Takeda Process (48).

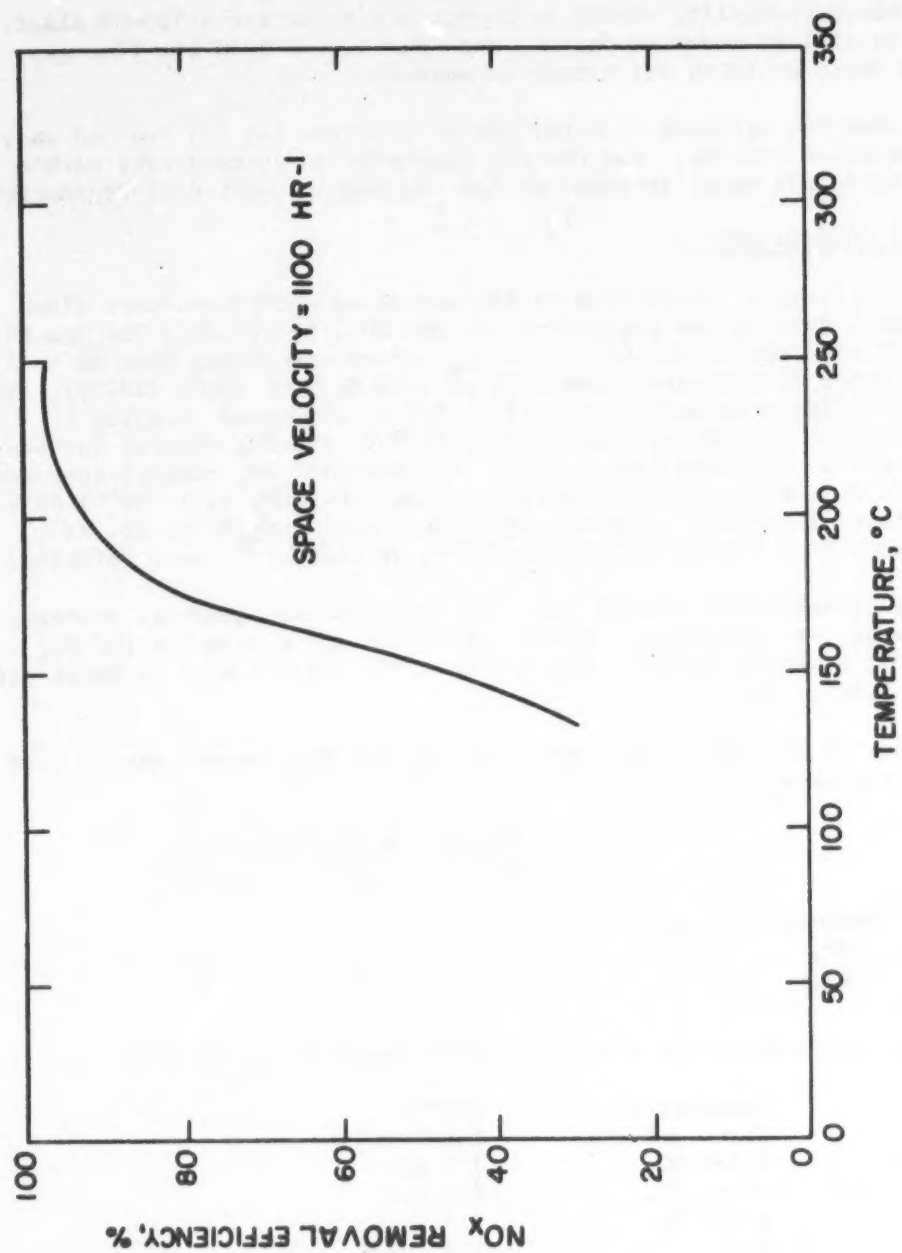


Figure 102. Relationship of Temperature and NO_x Removal Efficiency for Takeda Process (48).

to reach reaction temperature, however. If there was no FGD, the only consideration would be if there is enough space to place the Takeda system on the present site. It could be installed past the air heater and very little reheat would be required to reach reaction temperature.

The turndown capability should be acceptable since for a 500-MW plant, several trains will be required for NO_x and SO_2 removal from the flue gas, and reactors would be taken off stream as needed.

The information obtained on materials of construction has applied only to the regeneration systems. The heating regeneration process uses carbon steel while stainless steel is required for the washing method of regeneration.

Environmental Considerations

Data on NO_x removal efficiency versus operating conditions were given for experimental data on gas containing 300 ppm NO_x , 50 ppm SO_2 , 300 ppm NH_3 , 4-5% O_2 , 9-11% H_2O , and 10-11% CO_2 . The NO_x removal decreased from 98 to 85% as the space velocity increased from 1000 to 4000 hr^{-1} at 250°C (482°F). The NO_x removal efficiency decreased from 95 to 55% as the space velocity increased from 1000 to 4000 hr^{-1} at 200°C (392°F). The NO_x removal increased with an increase in reaction temperature. For example, NO_x removal increased from 40 to 80% as the temperature increased from 150-200°C (301-392°F) as a space velocity of 1100 hr^{-1} . Removal efficiency went from 80 to 95% as temperature rose from 200 to 250°C (392-482°F) at 1100 hr^{-1} space velocity.

Takeda's process also removes SO_2 . The SO_2 removal, however, decreased with an increase in temperature. With a 1100 hr^{-1} space velocity the SO_x removal was 95% at 200°C (392°F), and 80% at 250°C (482°F) with an inlet gas SO_x concentration of 50-150 ppm.

The effect of $\text{NH}_3:(\text{NO}_x + \text{SO}_x)$ ratio on NO_x and SO_x removal may be seen in the following data.

	<u>$\text{NH}_3:(\text{NO}_x + \text{SO}_x)$ mol ratio</u>		
	0.8	1.0	1.2
Removal efficiency, %			
NO_x	87	93	96
SO_x	76	84	90

The conditions under which the above data were taken are as follows:

Temperature	220°C
Space velocity	1,000 hr^{-1}
Inlet NO_x	200 ppm
Inlet SO_x	500 ppm
Inlet O_2	15% (vol)
H_2O	10% (vol)

Waste disposal problems would primarily depend on the method of regeneration used. In the washing method, a solution of CaSO_4 would have to be handled. In the heating method, any waste streams from an H_2SO_4 plant would have to be treated.

Critical Data Gaps and Poorly Understood Phenomena

Further details required about the Takeda process include the capital and operating costs for the regeneration system, and the operating conditions for the regeneration system. The catalyst consumption rate and NH_3 level in the treated gas are also not reported.

Advantages and Disadvantages

The advantages and disadvantages of the Takeda system are as follows:

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >90% NO_x removal efficiency
3. Produces marketable byproduct (98% H_2SO_4)

Disadvantages

1. Requires significant amounts of energy for the regeneration step (may require regeneration every 15 hr for treating coal-fired flue gas)
2. Requires somewhat clean (degree of particulate removal required is uncertain) gas feed
3. Requires auxiliary heater to attain or control reaction temperature
4. Has a low space velocity in the reactor ($<5000 \text{ hr}^{-1}$)

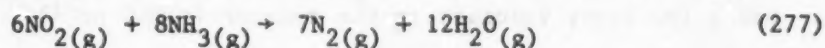
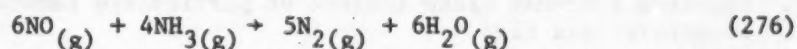
UBE PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (109)

The Ube (Ube Industries, Ltd.) process is a dry NO_x-only removal system based on the SCR of NO_x using NH₃. By inserting any one of the three different types of catalyst (B-2, SO_x-free; KV, low SO_x; or K-2, moderate SO_x levels) developed by Ube, this process can be specifically designed for the particular flue gas conditions. The K-2 catalyst, which is now considered the best Ube catalyst for treating coal-fired flue gas, was developed for treating flue gas containing a maximum of approximately 1000 ppm SO_x. Thus, although Ube apparently does not have a catalyst available for treating coal-fired flue gas containing 2400 ppm SO_x, the Ube process will be described assuming that the K-2 catalyst is being used.

This dry SCR process is very similar to the other dry processes in that it consists of three distinct sections: particulate removal, NH₃ injection, and catalytic reduction. The basic outline of the Ube process can be seen in the block flow diagram given in Figure 103.

The flue gas from the economizer at 350-400°C (660-750°F) passes through a hot ESP to remove 99% of the incoming particulates before entering the NH₃ mixing chamber. Gaseous NH₃ is injected into this mixing chamber at an NH₃:NO_x mol ratio of (1.0-1.1):1 and immediately mixed with the flue gas before entering the catalytic reduction reactor. As this gas mixture passes through the packed-bed reactor at approximately 350°C (660°F), the NO_x is selectively reduced to N₂ by the following reactions.



Since NO represents 90-95% of the NO_x in the flue gas, reaction (276) is the primary reaction occurring in the reduction reactor.

The clean flue gas from the reactor passes through the boiler air heater and then the FGD section before exiting through the stack.

Status of Development

Very little information has been released concerning the development of the Ube process. From preliminary information it appears that this process, using the K-2 catalyst, has been tested in a pilot plant treating 10,000 Nm³/hr of tail gas from an HNO₃ plant. During the first 8 mo of operation treating flue gas containing 3000 ppm NO_x and no SO₂, the Ube process was able to maintain 95% removal of NO_x with no decrease in catalyst activity.

No information has been published concerning any test results from treating either coal-fired flue gas or any other type of flue gas containing

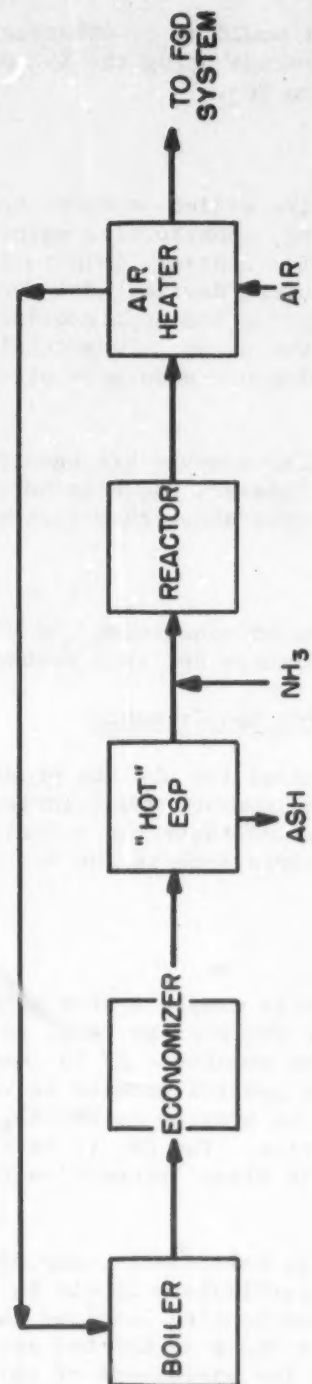


Figure 103. Flow Diagram of Ube Industries Process.

more than 700 ppm SO₂. The size of the test facility treating flue gas containing 700 ppm SO₂ and 300 ppm NO_x has not been released.

The next stage of development would be to construct a pilot plant to demonstrate the ability of this process using the K-2 catalyst to treat flue gases containing more than 1000 ppm SO₂.

Background of Process Developer

Ube is a relatively large, diversified Japanese chemical company with interest in chemicals, shipbuilding, construction materials, and transportation. Ube entered the air pollution control field in the early 1970's with the development of particulate control devices, both wet and dry, and a wet FGD system. In 1973 Ube began testing the applicability of base-metal catalysts for removing NO_x from exhaust gases. This catalyst research led to the Ube Industries SCR process which has undergone pilot-plant testing for the past year.

At the present time no American company has been licensed by Ube to market this process in the U.S. However, Ube does have a liaison office in New York City through which inquiries about this process are handled.

Published Economic Data

No information has been released concerning the total capital investment or the annual revenue requirements for this system.

Raw Material, Energy, and Operation Requirements

The major raw materials required for the Ube process are NH₃ and the base-metal catalyst. Utility requirements would include electricity, steam, and cooling water. The quantities of these raw materials and utilities and also the other operating requirements such as the operating personnel have not been published.

Technical Considerations

The Ube process is a relatively simple system with only five pieces of process equipment: a hot ESP, an NH₃ storage tank, an NH₃ vaporizing tank, a mixing vessel, and the reduction reactor. As is common for the dry SCR processes, the only major process control problem is vaporizing and injecting the exact amount of NH₃ required to provide an NH₃:NO_x mol ratio of (1.0-1.1):1 in the reduction reactor. The NH₃ to be injected into the system is metered into the mixing tank in direct proportion to the amount of flue gas passing through the system.

The NO_x removal efficiency is relatively independent of the inlet flue gas providing that the incoming particulate levels in the gas are very low. Although the maximum allowable particulate loadings have not been published, the use of small diameter pellets and a packed-bed arrangement in the reduction reactor seriously undermine the usefulness of this process for treating

coal-fired flue gas. Its ability to treat coal-fired flue gas, even with a very efficient hot ESP, without plugging seems highly questionable. At the present time Ube is modifying their process before testing begins on oil-fired boiler flue gas containing higher dust levels.

The catalytic reduction reactor will be the largest piece of process equipment in the Ube system and is a packed-bed type reactor. The catalyst particles are small pellets with typical dimensions of 5 mm in dia and 5 mm in height. Thus, for 90% NO_x removal the operating conditions in the reduction reactor would be the following:

Parameter	Value
NH ₃ :NO _x mol ratio	(1.0-1.1):1
Temperature	400°C (750°F)
Space velocity	5,000 hr ⁻¹
Catalyst size-shape	5 mm dia x 5 mm high pellet
SO _x level	2,400 ppm
Dust level	Small dust content

Under these conditions the lifetime of the catalyst is expected to be >8000 hr (1 yr).

This process would be difficult to retrofit onto an existing power plant equipped with cold ESP. The ductwork modifications required to remove and return the flue gas between the economizer and the air heater would be expensive. Thus, for retrofit applications, the flue gas will be removed after the existing cold ESP and passed through a countercurrent heat exchanger. The incoming flue gas is heated by extracting waste heat from the clean flue gas exiting the denitrification section. The inlet flue gas is further heated in an oil-fired furnace to raise the temperature to 400°C (750°F) and then mixed with gaseous NH₃ before the mixture enters the reduction reactor. From the reactor the flue gas passes to the heat exchanger to preheat the incoming flue gas before the gas enters the desulfurization section. Thus, the retrofitting of this system on existing power plants will increase both the capital and operating cost since extra equipment and fuel will be required.

Although the number of separate denitrification trains needed for a 500-MW boiler has not been disclosed, it is assumed that several trains will be required and the flue gas will be sent to either train through a common plenum. This type of arrangement will allow the denitrification system to partially cycle with the boiler availability by simply closing off any combination of trains. The major consideration during turndown is to maintain a temperature of 350°C in the reactor area to prevent the formation and precipitation of NH₄HSO₄ on the reactor internals.

Ube has not published any information on the materials of construction required for this system.

Environmental Considerations

The Ube process, during pilot-plant testing on HNO_3 tail gas (no SO_x or particulates) was capable of selectively reducing 90-95% of the NO_x . This high NO_x removal efficiency is dependent on both the reactor temperature remaining above 370°C (698°F) and the mol ratio of $\text{NH}_3:\text{NO}_x$ remaining in the range of 1.0:1 to 1.1:1.

This process is designed specifically for the selective removal of NO_x and does not remove any other pollutants from the flue gas.

Critical Data Gaps and Poorly Understood Phenomena

Many of the critical data gaps for this process involve the operating requirements and costs for this system. Ube has not released information on the capital or operating costs, catalyst consumption, utility requirements, pilot-plant data, materials of construction, or operation requirements and only scant data to determine status of development.

Advantages and Disadvantages

Advantages and disadvantages for the Ube process are listed below.

Advantages

1. Achieves >90% NO_x removal efficiency

Disadvantages

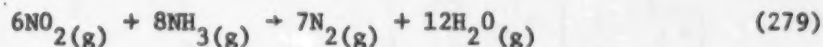
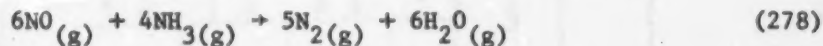
1. Has not been tested on coal-fired flue gas
2. Requires clean (SO_2 - and particulate-free) gas feed

UNITIKA PROCESS - DRY, SCR (NO_x-SO_x)

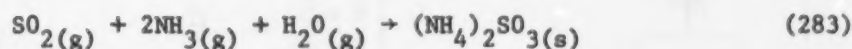
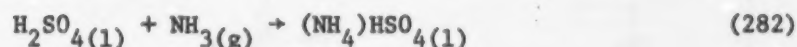
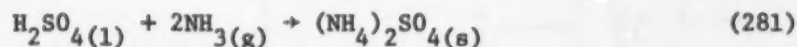
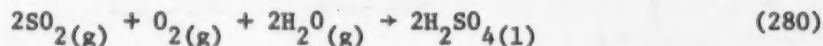
Process Description and Principles of Operation (2, 4, 46, 112)

Unitika has been developing two types of NO_x removal systems, a simultaneous NO_x-SO_x and an NO_x-only removal unit. The simultaneous NO_x-SO₂ removal process is considered almost fully developed by Unitika and is herein described.

Unitika's system passes the flue gas, having already passed through a particulate removing device and heated to the relatively low reaction temperature of 200-250°C (392-482°F), through a packed tower containing fixed C beds. The SO₂ in the flue gas reacts to form several products which are removed by adsorption in the C catalyst while the NO_x is reduced by NH₃ to N₂ which is removed with flue gas exiting the reactor. An assumed flow scheme for coal-fired FGT, based on the pilot-plant process flow, is depicted in Figure 104. The NO_x is converted to N₂ by NH₃ as follows:



There are several SO₂ removal reactions and all the products from the reactors are diffused and adsorbed into the catalyst. The reactions are as follows:



At 200°C (392°F) or above, reaction (280) is predominant while at below 180°C (356°F) reactions (281-284) take priority.

It should be noted that NH₃ is also involved in the SO₂ removal as well as NO_x removal. Unitika applies the following equation for required NH₃ consumption:

$$\text{NH}_3 = 0.8\text{NO} + (0.3-0.5) \text{SO}_x$$

Greater than 90% SO_x and NO_x removal is claimed.

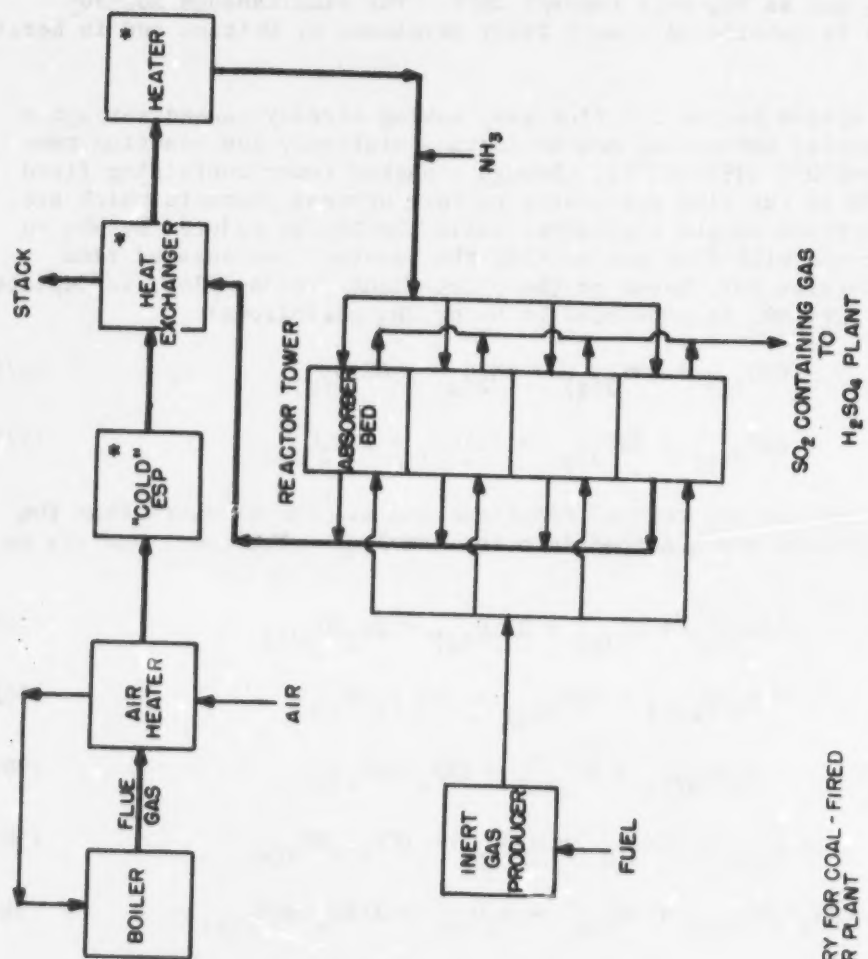
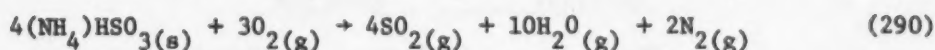
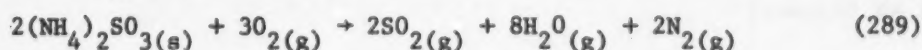
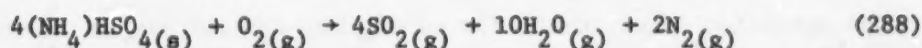
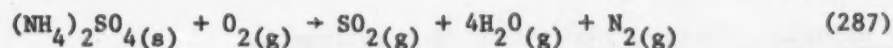
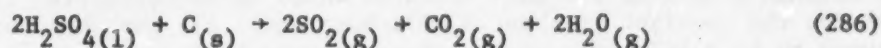
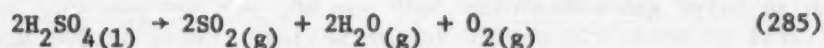


Figure 104. Flow Diagram of Unitika, Ltd. Process.

When the C bed becomes saturated, it is removed from the process and a regenerated bed is placed onstream. The C is regenerated in the presence of a low-O₂ gas at 300-350°C (572-662°F). The SO₂ is released for H₂SO₄ production as the SO₄⁼ and SO₃⁼ are decomposed to SO₂ and N₂ as follows:



At a 4500 Nm³/hr (1.5 MW equiv) capacity pilot plant, a packed tower consisting of four compartments with fixed C beds is utilized in treating gas containing 400 ppm SO₂ and 500 ppm NO_x. Three compartments are fed with flue gas while the fourth is being regenerated. The total tower height is 12 m and the C bed height is 0.6 m. The pressure drop is <100 mm H₂O. The space velocity is 1000 hr⁻¹ and NH₃ is injected to give about 600 ppm in the flue gas. The adsorption time is 24 hr and regeneration time is 8 hr. The SO₂ concentration in the gas from regeneration is 5-10%.

The C consumption is given as about 50% of a charge per year. The C is said to hardly deteriorate and is resistant to damage by SO_x and particulate matter. The catalyst life exceeds 1 yr.

Status of Development

Unitika began developing an SO_x removal process in 1971. This removal technique with activated C was evaluated with a 150 Nm³/hr and a 600 Nm³/hr capacity models. When NO_x removal became necessary, Unitika incorporated NO_x removal into the SO_x removal process. A pilot plant of 4500 Nm³/hr flue gas capacity with an inlet composition of 500 ppm NO_x and 400 ppm SO₂ is currently in operation at Union Glass Industry Company, Ltd., at Hirakata, Japan.

Background of Process Developer

Unitika, Ltd., has a liaison office in New York. This should make Unitika's process accessible to the U.S. market. Based on the successful results of the pilot plant at Union Glass, a larger NO_x-SO₂ removal plant will be erected.

Published Economic Data

The capital investment for a simultaneous NO_x - SO_2 removal system and resulting acid recovery section treating 500,000 Nm^3/hr (167 MW equiv) of flue gas is reported to be \$10M or about \$60/kW (46). The revenue requirement, with an inlet gas containing 1000 ppm SO_x and 300 ppm NO_x , is equivalent to \$27.3/kl of heavy oil burned in the boiler. Using 12,000 $\text{Nm}^3 = 1$ kl of oil, the revenue requirement equals \$1138/hr which is 6.8 mills/kWh (46). The cost for the catalyst is about \$3800/short ton. All the above values are assumed to be based on a Japanese location and 1976 costs.

Raw Material, Energy, and Operation Requirements

The estimated requirements for an NO_x - SO_2 removal system treating a 500,000 Nm^3/hr stream of flue gas containing 1000 ppm SO_x and 300 ppm NO_x are as follows:

<u>Material</u>	<u>Quantity</u>
NH_3	13.3 short tons/day
Fuel, LPG	55.5 short tons/day
Electricity	2,708 kW

The electrical demand is equal to 1.62% of the equivalent total output of the plant.

No information on requirements for the H_2SO_4 production are available, along with operating, maintenance, and technical support needs. However, the H_2SO_4 manufacturing needs and costs should be the same as for the production of industrial-grade H_2SO_4 made by the contact process method.

Technical Considerations

Compared to wet systems, this system is simple with a packed tower reactor and regeneration gas producer. It is slightly more complex than some other dry processes since a system for handling SO_2 -rich gas from regeneration for H_2SO_4 production is included.

The NO_x and SO_2 removal, and consequently, absorption and regeneration cycles will be affected by inlet gas composition. On a pilot plant with 400 ppm SO_2 and 500 ppm NO_x in the flue gas, absorption time is 24 hr with an 8-hr regeneration time for 90% NO_x - SO_x removal. Data with inlet NO_x of 200 ppm and SO_x of 1000 ppm, showed NO_x removal still about 90% after 4 days, but SO_x removal had fallen below 90% after only 22 hr. With coal-fired flue gas which would contain about 2400 ppm SO_x , the regeneration frequency should be significantly greater than that just mentioned due to the richer SO_x content in the flue gas.

Although the reaction temperature is lower than most dry NO_x removal systems, the space velocity is only 1000 hr^{-1} and the reactors would probably

be considerably larger than for other processes. Also, more reactor area is required since part will be undergoing regeneration.

Unitika's process should be suitable for retrofit in the case of a plant without FGD. A small amount of heat is required but not as much as other processes whose reaction temperature is 300-400°C (572-752°F). The minimum land required for a 500,000 Nm³/hr (167 MW equiv) gas treatment facility is 4000 m².

This simultaneous NO_x-SO₂ process should provide adequate turndown capacity. This could be handled by simply removing absorption beds from use.

Carbon steel is probably the major material of construction.

Environmental Considerations

SO₂ removal is much more sensitive to space velocity than NO_x removal. At 240°C (464°F) and a space velocity of 1000 hr⁻¹, the SO₂ removal was 93% and it decreased to 86% with an increase in space velocity to 1400 hr⁻¹ at a constant temperature. The NO_x removal varied from 95 to 80% as the space velocity increased from 2000 hr⁻¹ to 2700 hr⁻¹. An increase in temperature decreased the SO₂ removal. An SO₂ removal of 98% at 200°C (392°F) with space velocity of 1000 hr⁻¹ was decreased to 93% as the temperature increased to 240°C (464°F) at the same space velocity. The relationship of SO₂ removal and NO_x removal to temperature and space velocity are given in Figures 105 and 106.

SO₂ is removed along with NO_x in Unitika's system. The SO₂ is released after regeneration and the SO₂-rich gas is used in producing a high-purity H₂SO₄.

There should be no waste-disposal problems except for possible exhaust gases during the making of byproduct from the SO₂-rich regeneration gas.

No data are given on effects of Cl⁻ upon this process. There are no apparent work hazards.

Critical Data Gaps and Poorly Understood Phenomena

The information lacking on this process includes the operating manpower, maintenance, and technical support requirements. The expected NH₃ emissions in the treated gas and the maximum particulate level allowed in the inlet flue gas have not been reported.

Advantages and Disadvantages

The advantages and disadvantages of the Unitika simultaneous NO_x-SO₂ removal system are as follows:

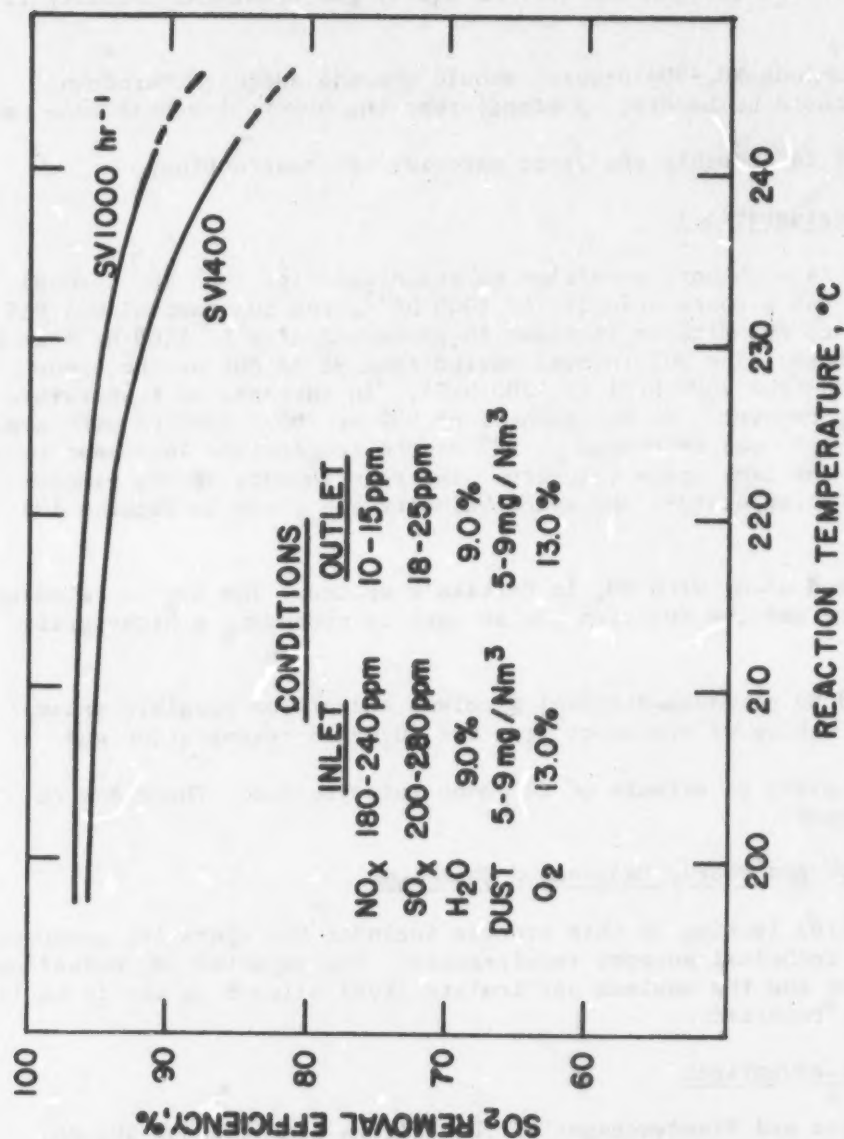


Figure 105. Relationship of SO₂ Removal Efficiency to Reaction Temperature and Space Velocity for Unitika Process (46).

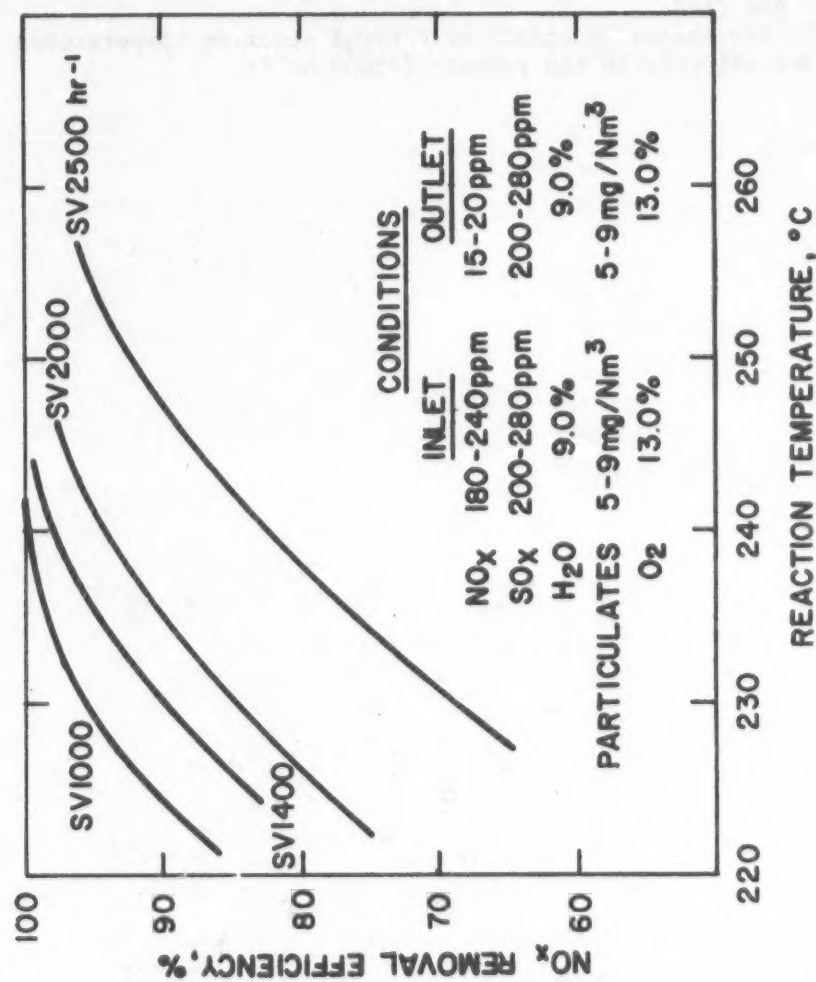


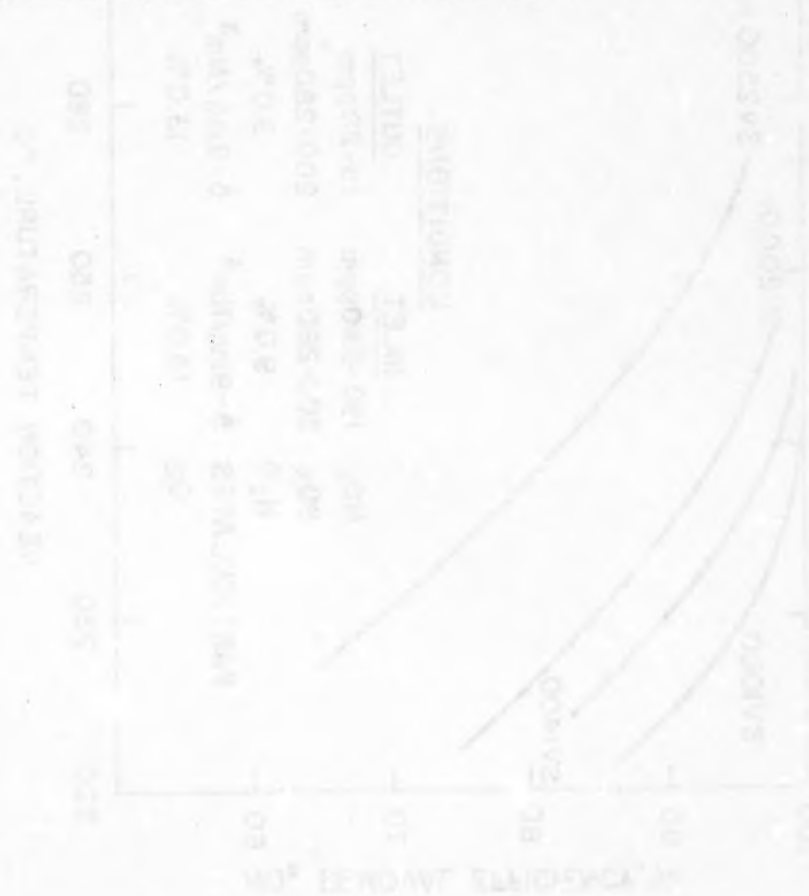
Figure 106. Relationship of Reaction Temperature and Space Velocity on NO_x Removal Efficiency for Unitika Process (46).

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves $>90\%$ NO_x removal efficiency
3. Produces marketable byproduct (H_2SO_4)

Disadvantages

1. Requires significant amounts of energy for the regeneration step
2. Has not been tested on coal-fired flue gas
3. Requires somewhat clean (degree of particulate removal required is uncertain) gas feed
4. Requires auxiliary heater to attain or control reaction temperatures
5. Has a low space velocity in the reactor ($<5000 \text{ hr}^{-1}$)



UNITIKA PROCESS - DRY, SCR (NO_x)

Process Description and Principles of Operation (46)

In addition to the simultaneous NO_x-SO₂ removal system, Unitika, Ltd., has developed an NO_x-only removal process. Though details about the process are unavailable, it is known to be an SCR process. More information should be reported in the near future. The NH₃:NO_x mol ratio is (1.0-1.1):1 and reaction temperatures range from 320-410°C (590-770°F). Information concerning the catalyst composition is not available. NO_x removal efficiencies of >90% have been achieved on bench-scale tests.

Status of Development

Unitika has applied this NO_x-only method on 150 Nm³/hr (0.05 MW equiv) capacity tests for 45 days and 200 Nm³/hr (0.07 MW equiv) flue gas capacity tests for 300 days. This technology is to be tested during 1977 with equipment capable of treating 70,000 Nm³/hr (23 MW equiv) of flue gas.

Background of Process Developer

Unitika has a liaison office in New York which should make this process available to the U.S. market.

Published Economic Data

The estimated capital investment for the NO_x removal system capable of treating 500,000 Nm³/hr (167 MW equiv) of flue gas is \$4M or about \$24/kW (46). The revenue requirement for this facility with 300 ppm NO_x in the inlet gas is \$8.60/kl of oil. Assuming a kl of oil = 12,000 Nm³ of gas, the revenue requirement is about 2.1 mills/kWh (46). All of the above values are assumed to be based on a Japanese location and 1976 costs.

Raw Materials, Energy, and Operation Requirements

The estimated consumption of these for an NO_x removal system handling 500,000 Nm³/hr of flue gas containing 1,000 ppm SO_x and 300 ppm NO_x is as follows:

<u>Material</u>	<u>Quantity</u>
NH ₃	3 short tons/day
Fuel	16.7 short tons/day
Electricity	917 kW

Hence, the electrical requirement represents 0.55% of the total equivalent plant output, assuming 3000 Nm³/hr = 1 MW. Operating manpower, maintenance, and technical support needs are not available.

Technical Considerations

Data from NO_x removal bench-scale tests, indicate the NH₃:NO_x mol ratio ranges from 1:1 to 1.1:1 and the reaction temperature varies from 320-410°C (590 to 770°F). The space velocity tested varied from 10,000 to 15,000 hr⁻¹. The NO_x removal essentially remained constant at 90-92% during 45-day operations at inlet gas SO_x concentration of 100-1000 ppm and also for 360 ppm SO_x levels for a 300-day-long test. The conditions and results of three bench-scale tests are shown in Table 29.

TABLE 29. BENCH-SCALE TEST CONDITIONS FOR UNITIKA (NO_x) PROCESS (46)

	Catalyst name		
	UL-3	UL-2	UL-2
Test duration, days	300	45	45
Gas flow rate, Nm ³ /hr	200	150	150
Space velocity, hr ⁻¹	15,000	10,000	10,000
Inlet NO _x , ppm	180	180	300
Inlet SO _x , ppm	360	1,000	100
Reaction temperature, °C	370-410	320-380	340-360
NH ₃ :NO _x mol ratio	1.1:1	1:1	1:1
NO _x removal efficiency, %	90-92	90-92	90-92

With the high space velocities employed in this process, the size of the reactor should be slightly smaller than most SCR processes using 300-400°C reaction temperatures. The majority of the construction material for equipment will probably be carbon steel.

Environmental Considerations

The only information obtained concerning environmental considerations is on sensitivity of NO_x removal to operating conditions as given in Table 29.

Critical Data Gaps and Poorly Understood Phenomena

The data gaps include the following areas.

1. Process flow scheme and process control plan
2. Development history and present status
3. Operating manpower, maintenance, and technical support requirements
4. Retrofit applicability and turnaround capability
5. Catalyst composition and shape
6. Waste disposal requirements
7. NH₃ emissions in outlet gas
8. Maximum particulate level allowed

Advantages and Disadvantages

The advantages and disadvantages of the Unitika process for removal of NO_x only are as follows:

Advantages

1. Achieves $>90\%$ NO_x removal efficiency

Disadvantages

1. Has not been tested on coal-fired flue gas
2. Has been tested only in a bench-scale unit
3. Requires somewhat clean (degree of particulate removal required is uncertain) gas feed

UNIVERSAL OIL PRODUCTS PROCESS - SHELL CuO PROCESS - DRY, SCR (NO_x-SO_x)

Process Description and Principles of Operation (92, 93)

Universal Oil Products, Inc., (UOP) offers a dry simultaneous NO_x-SO_x removal process using the Shell CuO process. The SO₂ in the flue gas reacts with CuO to form CuSO₄ and the SO₂ is released later during a regeneration step to be used in alternative ways. In the presence of the CuO and CuSO₄ catalysts, NO_x is reduced to harmless N₂ and H₂O by reaction with NH₃. Two or more reactors are needed because while NO_x and SO_x removal (the acceptance stage) is underway in one reactor, regeneration of the catalyst in the swing reactor is being performed.

A proposed flow scheme for treating flue gas from a commercial-scale coal-fired boiler is shown in Figure 107. The flue gas leaving the boiler-economizer at about 400°C (750°F) has NH₃ injected into the gas stream and proceeds to a reactor in the acceptance stage. The reactor contains a fixed bed of the parallel-passage design. The flue gas passes through the parallel-passage reactor by flowing across the face of the acceptor material and not through it. The acceptor material is Cu on a special Al₂O₃ support. The Cu is rapidly oxidized to CuO upon introduction of the flue gas to the reactor as follows:



The SO₂ in the flue gas reacts with this CuO to form CuSO₄ as shown below:



The CuSO₄ is a catalyst for the reduction of the NO_x in the flue gas by combining with NH₃ to create N₂ and H₂O as follows:



The treated flue gas then leaves the reactor and passes through the air heater and particulate removal equipment, such as an ESP, before going to the stack.

When the acceptor material becomes saturated with the SO₂ so that the removal efficiency attains the limiting value, the flue gas flow is diverted to a reactor containing regenerated acceptor material. The spent acceptor is regenerated with a steam-diluted, H₂-containing regeneration gas which may be produced, for example, for steam-naphtha reforming or coal gasification. This regeneration occurs at the same temperature of 400°C as acceptance. Therefore, heating or cooling of the acceptor is not required. The CuSO₄ is converted to elemental Cu, SO₂, and H₂O, while any unreacted CuO is reduced to Cu and H₂O. The following equations express the above reactions.

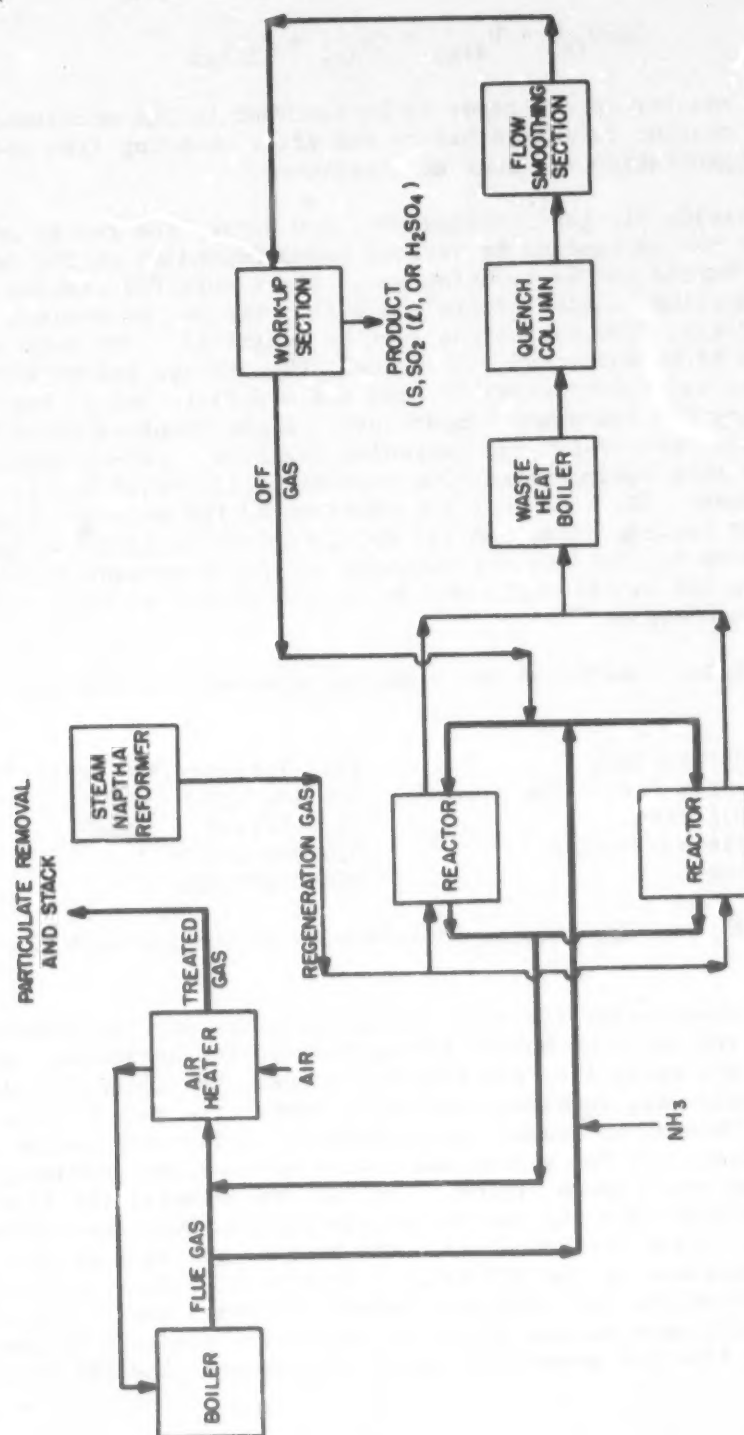
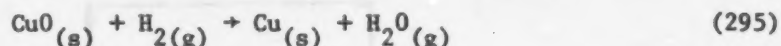
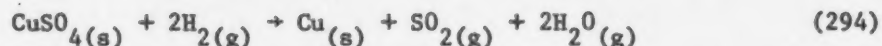


Figure 107. Flow Diagram of UOP Process.



The regenerated reactor is now ready to be returned to the acceptance operation mode. The reactor is purged before and after changing from modes of acceptance to regeneration and back to acceptance.

The regeneration off-gas contains SO_2 , H_2O vapor, and traces of unreacted reducing gas and may be handled by various means depending on the desired product and the inerts in the reducing gas. Since this FGT process is cyclic, the off-gas production is also cyclic and before further processing of the regeneration off-gas, flow variations must be minimized. The bulk of the H_2O vapor also needs to be condensed. Therefore, the off-gas passes through a waste heat boiler to recover sensible heat and a direct-contact cooler for heat removal below the dew-point temperature. A gas-compressor/gas-holder is considered the simplest system for dampening the flow. SO_2 -concentrated gas is released from this equipment on flow control to either of the following production purposes: (1) elemental S production by the modified Claus method, (2) liquid SO_2 by liquefaction, and (3) H_2SO_4 production by oxidation. The choice of the above methods for regeneration off-gas treatment is primarily economic. Figure 108 exhibits the option for the workup sections for the SO_2 -rich regeneration off-gas.

Normal operating conditions which may be expected for this process are as follows:

Maximum particulate	Full loading (≥ 10 gr/sft ³)
Pressure drop across the reactor	5-6 in. H_2O
$\text{NH}_3:\text{NO}_x$ mol ratio	(1.0-1.2):1
Average space velocity	5,000-8,000 hr ⁻¹
Temperature	400°C (750°F)

UOP states that NO_x and SO_x removal efficiencies of 90% for each may be achieved.

There are several other important characteristics of this process. With this FGT system tied into the boiler system between the economizer and air heater, the most practical flue gas reaction temperature control method, though not the only way, involves regulating either the flow of flue gas or boiler feedwater through or around the exchanger. This controls the heat transfer rate. Also, the FGT system and boiler may operate independently of each other with an open bypass system. The FGT system pulls the flue gas from the flue gas duct into its fan and expels the gas into the header to which the reactor inlets are connected. The treated gas then returns to the flue gas duct downstream of the FGT inlet. With no flow restriction in the flue gas duct between the FGT inlet and return, a bypass around the FGT unit is created. A continuous stream of gas is fed to the reactors by the FGT fan regardless of the flue gas generation rate. Any excess flue gas from the

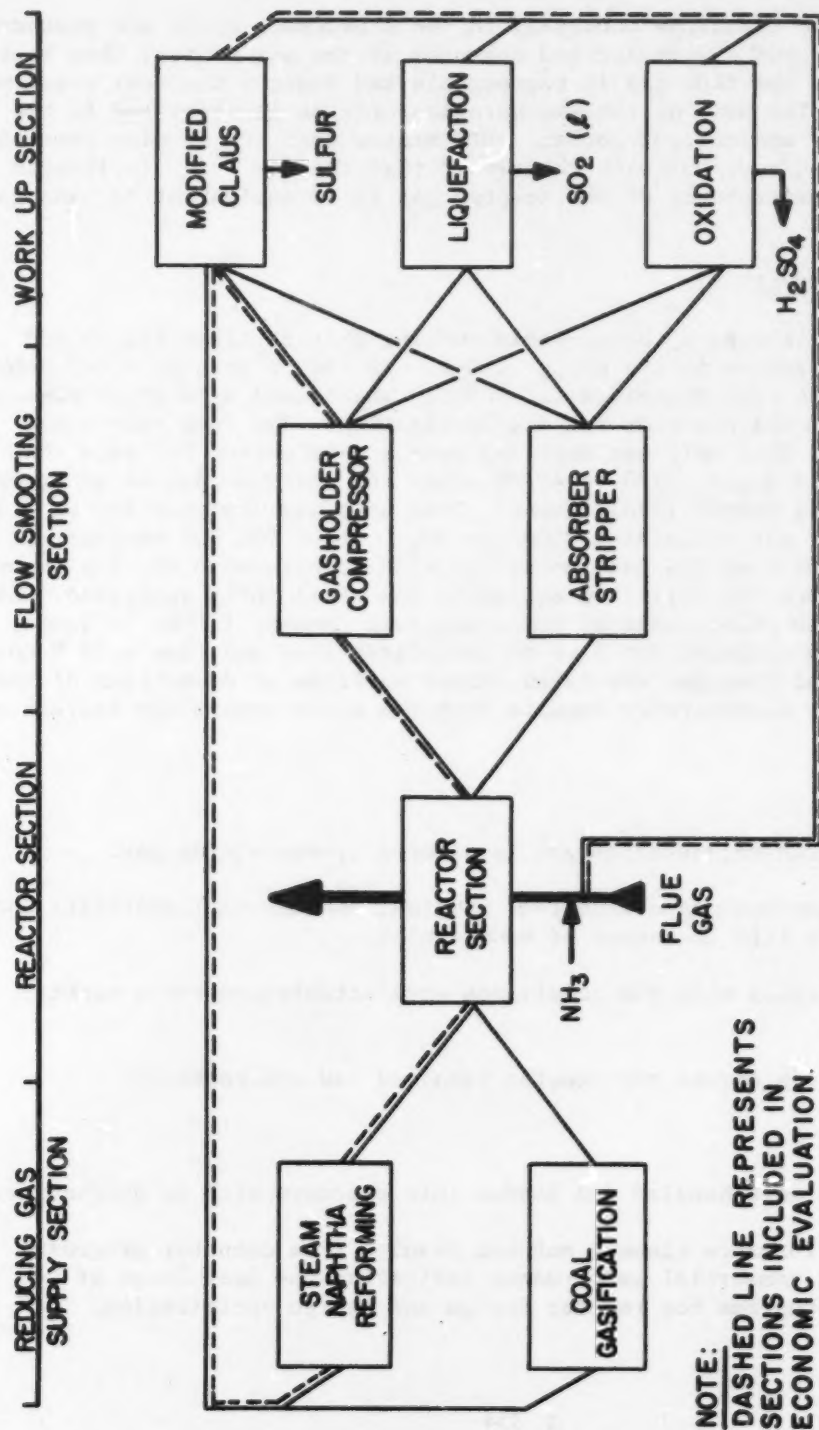


Figure 108. Diagram of Alternative Methods Used With UOP Process for the Following Sections:
 (1) Regeneration Gas Supply, (2) Flow Smoothing, and (3) Workup Section (92).

boiler above the FGT fan rate may bypass the FGT system while gas may be recycled from the FGT discharge to the FGT fan inlet if the flue gas produced in the boiler is less than the FGT fan rate.

Also, all the reactions occurring in the acceptance cycle are exothermic, and by having the FGT system located upstream of the air heater, this heat of reaction added to the flue gas is recoverable and reduces the fuel required for the boiler. The heat of the regeneration off-gas is recovered in the waste heat boiler and contact cooler. UOP states that SO_3 is also removed by the Cu-on- Al_2O_3 acceptor with the result that the dew point is lowered allowing stack temperatures of the treated gas to be equivalent to flue gas from low S fuels.

Status of Development

Shell began laboratory bench-scale testing on a catalyst search and desulfurization process in the early 1960's. In 1967 a unit of 0.2-0.3-MW capacity was built near Rotterdam (at Pernis) which used a parallel-passage reactor and unit cell acceptor for desulfurization. The fuel source was high-S fuel oil. This unit was operated over a 4-yr period for more than 20,000 cycles. In August 1973, a 40-MW equiv FGD unit was placed on stream at Showa Yokkaichi Sekiyu (SYS), Japan. This unit was designed for an oil-fired boiler flue gas containing 2500 ppm SO_2 . About 90% SO_2 removal was obtained. This unit at SYS has functioned with simultaneous NO_x - SO_x removal since mid-1975 when NH_3 injection equipment was permanently installed. Also, a 0.6-MW equiv-FGD pilot plant of Tampa Electric Company (TECO) in Tampa, Florida, has been operated for 3 yr on coal-fired flue gas from 3.5% S coal. The slip stream of flue gas was taken either upstream or downstream of the ESP. Some of the demonstrated results from the above operations include the following:

Pernis

- The preferred regeneration gas is diluted H_2 -containing gas.
- The acceptor possessed excellent physical and chemical stability and will have a life in excess of 8000 cycles.
- Corrosion rates with FGD conditions were established for a number of metals.
- Pressure drop across the reactor remained low and constant.

SYS

- Unit cells were handled and loaded into reactors with no difficulty.
- Actual performance closely matched results from computer programs simulating commercial performance indicating the usefulness of computer programs for reactor design and design optimization.

- Engineering scaleup consists mainly of paralleling standardized unit cells.
- The unit is operated by an automatic sequence controller requiring practically no operator attention after startup periods.
- Special valves functioned properly to isolate reactors during regeneration.
- Open bypass performs as intended to make FGT and boiler operations independent of each other.

TECO (In addition to some items already stated for SYS)

- Acceptor is chemically and physically stable after 13,000 cycles (equiv to a 3-yr life) with 90% SO₂ removal in 4-m bed and pressure drop of 5-6 in. H₂O.
- Process performed well with particulate loading equal to 10 gr/sft³ (about 23 gm/Nm³) (greater during soot blowing); in situ cleaning of reactor internals was required and developed.

Background of Process Developer

Shell International Petroleum Company developed this process and has been involved in the program since the early 1960's. The UOP Process Division holds the worldwide licensing rights to the Shell FGD process (with the exception of the Far East). The Shell FGD system is commercially available for oil-fired boilers. The simultaneous NO_x and SO₂ removal has been used at SYS unit since 1975 on an oil-fired boiler while the TECO pilot plant has operated on a coal-fired flue gas for 3 yr. This process is readily accessible to the U.S. market.

Published Economic Data

UOP estimates the total capital investment for a NO_x-SO_x removal system treating flue gas from a 500-MW plant to be about \$131/kW (92). The revenue requirement for this same 500-MW case is equiv to 5 mills/kWh (92). These values are based on mid-1977 costs with a midwestern U.S. location. The factors describing the above FGT system and providing the basis for the economics include the following:

Flue gas to reactors, Nm ³ /hr	1,657,000
Temperature of flue gas, °C	400
SO ₂ content, ppm	2,580
NO _x content, ppm	634
SO ₂ removal, %	90.5
NO _x removal, %	90.0

Number of reactors, accepting/regenerating	6/2
Bed length, m	6.0
Reactor diameter, m	7.38
Acceptance time, min	64.3
Acceptor quantity, kg/reactor	54,000
System pressure drop, cm H ₂ O	40

As indicated in Figure 108 there are a variety of combinations possible for the sections supporting SO_x removal. The dotted lines in this figure reveal the integrated units chosen for the above economic evaluation. The gas-compressor/gas-holder was chosen because of economics. The modified Claus system and steam-naphtha reforming unit were chosen because more information was available on these sections.

Raw Materials, Energy, and Operation Requirements

The amounts of raw materials and energy required for the same 500-MW case stated in Published Economic Data follow:

Material	Quantity
NH ₃	21 short tons/day
Electricity	7,712 kW
Steam, (net)	187 short tons/day
Naphtha	57.23 bbl/hr

The above steam requirements are based on 867 short tons/day steam usage for FGD and NH₃ injection and a steam credit of 680 short tons/day for the workup, modified Claus, and steam-naphtha units. The total electric usage represents 1.5% of the total equivalent power output of a power plant.

Also, a heat credit totaling 131 MBtu/hr is claimed by UOP. Sources of heat credit in the FGT section include fan compression, reaction heat from both acceptance and regeneration, and dew-point suppression.

For the 500-MW case, the labor and supervision needs were estimated to be 21,000-hr annually. At an average cost of \$8/hr, this equals \$168,000/yr. The maintenance costs were estimated to be about \$1,046,000, which is about 6% of the total annual revenue requirement. UOP states that for the 40-MW equiv unit at SYS, no additional manpower was needed. Excluding startup and initial operation period, the required operator attention was almost nil.

Technical Considerations

The UOP system is composed of several more operation steps than most dry SCR NO_x removal methods, since SO₂ processing equipment is needed for treating the regeneration off-gas. However, the units used in the UOP process involve proven technology and straightforward chemistry. Flue gas valves of large diameter are needed to provide tight seals at high temperatures and over

several thousand opening and closing cycles. These valves must separate the reactors undergoing acceptance or regeneration from the regeneration or main flue gas respectively. UOP states that the valves selected for this purpose have performed satisfactorily at SYS and TECO.

The NO_x and SO_x removal unit is controlled and protected with the use of an automatic sequence controller by setting the acceptance and regeneration cycle lengths, monitoring all valve positions, temperature, and flow rates. At SYS, the NO_x at the outlet of the FGT system is measured continuously by the chemiluminescence method and the $\text{NH}_3:\text{NO}_x$ ratio is controlled manually.

It should be noted that at the end of the regeneration period the acceptor is in the form Cu. With all the acceptor in this form and several minutes required for oxidation of the Cu to CuO , if NO_x removal were attempted at the beginning of the acceptance stage, the NO_x level in the treated gas would actually increase because of NH_3 conversion to NO_x . At SYS, NH_3 injection is automatically controlled to start a few minutes after the acceptance cycle is begun. More efficient methods recommended for a new design are as follows: (1) preoxidize the acceptor before introducing the flue gas and injecting NH_3 or (2) allow a portion of the acceptor bed to remain unregenerated as CuSO_4 . This second method may be the best solution.

The NO_x and SO_2 removal efficiencies are considered independent of inlet NO_x and SO_2 concentrations respectively. The NO_x reaction is first order and the NO_x reaction rate is directly proportional to the NO_x concentration. The NO_x removal rate will increase as bed length or cycle length increases.

The reactor size for this NO_x and SO_2 removal method should be about the same as other SCR processes with similar operating conditions. The number of reactors required for this Shell CuO process is greater than other SCR processes since the same vessel is used for both acceptance and regeneration. The ratio of reactors in the acceptance stage to those in the regeneration cycle for the 500-MW case is 6:2. However, this is a design variable, for example, if lower-S western coal had been the basis, the ratio would probably be 5:1.

In examining retrofit applicability, the UOP Shell CuO process with simultaneous NO_x and SO_x removal would require reheat equipment such as a heat exchanger and heater if installed after the air heater. The simultaneous NO_x - SO_2 removal process would not be suitable for retrofit on a plant with an existing FGD system. However, the UOP Shell CuO process can be operated in an NO_x -only removal manner as reported under a separate detailed process description.

With the open bypass system, the turndown ratio is unlimited, capable of operating from full boiler load to complete recycle. Naturally, operating with total recycle produces a decrease in reactor regeneration frequency.

The materials of construction are considered proprietary information; however, UOP states that no unusual materials are used. UOP has derived corrosion rates for various metals under FGD reactor conditions. Service life of at least 15 yr for the reactor internals has been estimated with the proper construction materials.

A marketable quality byproduct is manufactured by this process. Depending upon economics, elemental S, liquid SO_2 , or a concentrated SO_2 gas feed to an H_2SO_4 plant may be produced.

Environmental Considerations

An advantage of the UOP Shell CuO process is that it is capable of simultaneous NO_x and SO_2 removal. Data from tests at SYS with a 4-m bed are presented in Figure 109 showing the NO_x and SO_x concentration varying with time at different $\text{NH}_3:\text{NO}_x$ mol ratios at the reactor outlet. The SO_x concentration decreases rapidly from above 1200 ppm to below 100 ppm as Cu is converted to CuO which then reacts with SO_2 to form CuSO_4 . However, as CuO is changed to CuSO_4 , the SO_2 level in the treated flue gas rises to about 400 ppm after 120 min. The NO_x removal increases with cycle length as more Cu is converted to CuO and eventually CuSO_4 , the catalyst for the NO_x reduction reaction. The effects of $\text{NH}_3:\text{NO}_x$ ratio and the fraction of acceptor converted to CuSO_4 upon NO_x removal are indicated in Figure 110. These data are from similar tests at the SYS unit. A 90% removal of both SO_x and NO_x is expected with the use of a 5-m bed and by allowing 1 m to remain unregenerated; that is, the acceptor is in the CuSO_4 form for NO_x removal even at the first introduction of flue gas.

There is no significant waste disposal needed for this system other than that associated with the production of byproducts from the SO_2 . An environmental concern would be the leakage of excess NH_3 to the atmosphere; however, UOP claims NH_3 in the treated gas averages 1 ppm.

The parallel-passage reactor has been shown to be capable of operating at normal conditions with full particulate loading ($\geq 10 \text{ gr/sft}^3$). Initial testing with full flyash loading to the reactor at the Pernis unit showed no deterioration in performance. However, at SYS the high V- and Na-containing flyash gradually fouled the reactor internals forcing runs to be limited to operating periods of 1-2 mo. The higher particulate loading with coal-fired flue gas at TECO of 10 gr/sft^3 or greater caused a decline in performance after only days of operation. As a result of this problem, a procedure was developed and implemented at the Tampa pilot plant which provided in situ cleaning of reactor internals during normal operation. This technique allowed stable performance with high particulate loadings; pressure drop across the reactor and desulfurization were not affected. In situ cleaning of reactor internals will be implemented at SYS also.

Testing at TECO also demonstrated that Cl_2 and Cl^- in flue gas had no adverse effect upon the acceptor performance. The loss of Cu was negligible.

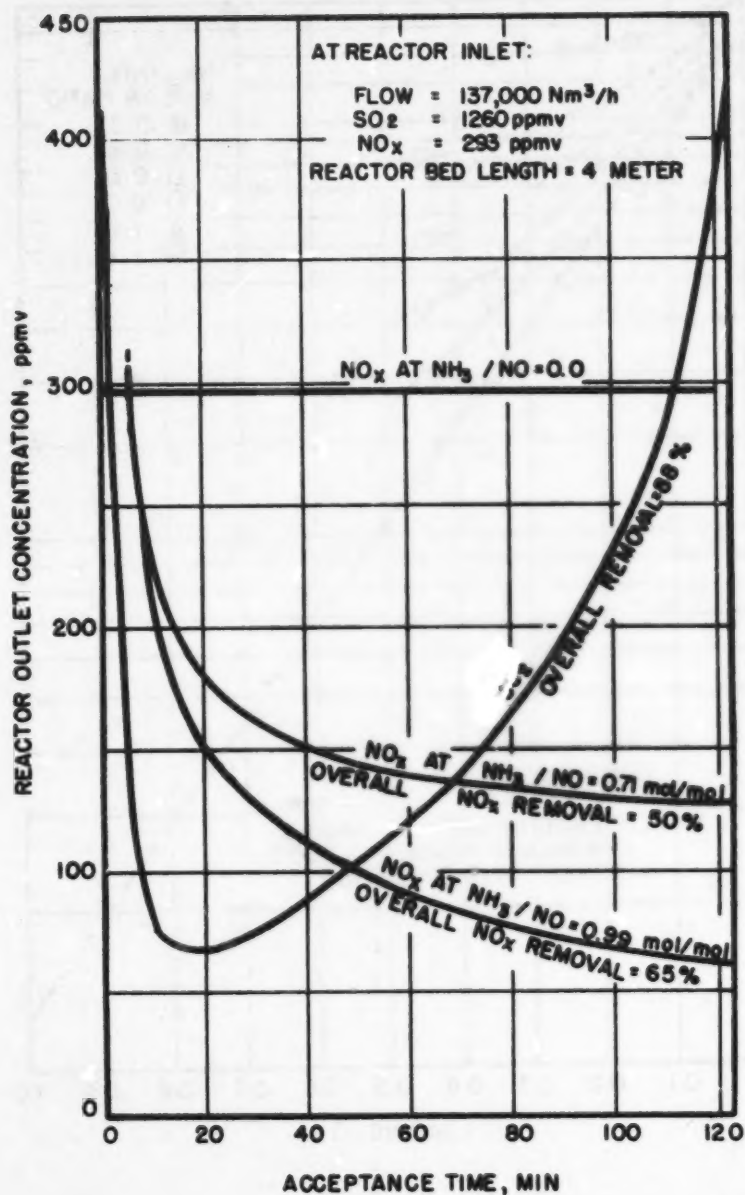


Figure 109. Performance of Shell FGD Reactor at SYS.
 Instantaneous SO₂ and NO_x Slip (92).

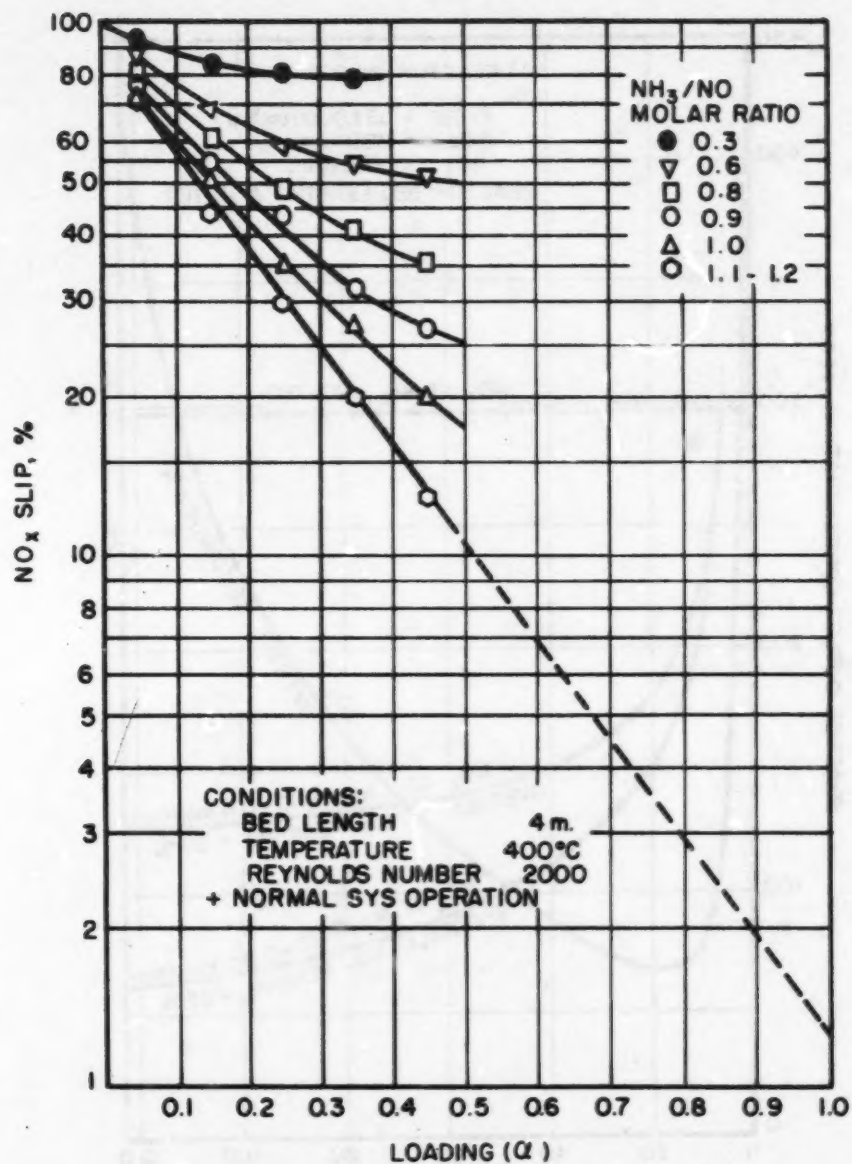


Figure 110. NO_x Slip, Percent of Intake vs Loading, $\text{CuSO}_4/(\text{CuO} + \text{CuSO}_4)$ Mol Ratio for a Commercial Shell-FED Absorber/Catalyst with UOP Process (92).

Since the regeneration gas contains H_2 , which may detonate with O_2 mixtures, the regeneration gas must be prevented from coming into contact with the main flue gas. The flammability limits for H_2 -air mixtures at atmospheric pressure are 4-74% H_2 (89). The reactor is purged before and after each regeneration cycle. Also, UOP states that since the H_2 -containing regeneration gas is diluted with steam, no detonation would result even in the case of failure of both the purge system and sequence control systems. With this extreme example, combustion may occur within the closed reactor which would raise the pressure from atmospheric to about 1.5 atmosphere, the design pressure for the reactor. Also, UOP feels the safety of this process is proven by the thousands of hours of safe operation.

Critical Data Gaps and Poorly Understood Phenomena

Although there are no major poorly understood phenomena, the use of an Al_2O_3 base for the $CuSO_4$ catalyst is questionable since there is a trend of competing processes to be changing to alternate, supposedly more stable supports. It is recognized that UOP refers to their catalyst as being on a "special" Al_2O_3 support.

Advantages and Disadvantages

The following are the advantages and disadvantages of the UOP-Shell CuO simultaneous NO_x - SO_x removal process:

Advantages

1. Removes NO_x and SO_2 simultaneously
2. Achieves >90% NO_x removal efficiency
3. Produces marketable byproduct (S, or H_2SO_4 , or $SO_2(1)$)
4. Has been applied to flue gas from commercial oil-fired boilers
5. Is a slight modification of a commercially available FGD system
6. Operates with full particulate loadings (>7 gr/sft³)
7. Claims <10 ppm by vol NH_3 in treated flue gas
8. Claims full turndown capability

Disadvantages

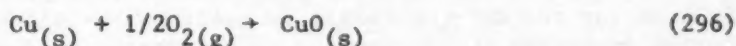
1. Has not been tested on coal-fired flue gas

UNIVERSAL OIL PRODUCTS PROCESS - SHELL CuO PROCESS - DRY, SCR (NO_x)

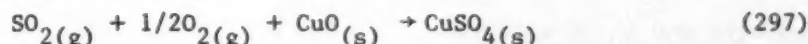
Process Description and Principles of Operation (92, 93)

In addition to simultaneous NO_x-SO_x removal, the Shell CuO process offered by Universal Oil Products (UOP) may be used for NO_x removal only. NO_x-only removal may be carried out by eliminating the regeneration step and subsequent SO₂ removal facilities from the Shell CuO simultaneous NO_x-SO_x removal process.

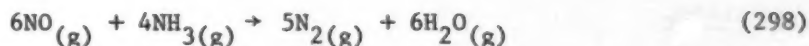
This process is depicted by the flow diagram in Figure 111. The flue gas leaves the boiler economizer and NH₃ is injected into the flue gas. The entire gas stream enters the fixed-bed, parallel-passage reactor. The reactor bed contains Cu (on special Al₂O₃) which, upon introduction of the flue gas to the reactor, is oxidized to CuO as follows:



The CuO then reacts with the SO₂ to form CuSO₄ according to the following:



The CuSO₄ acts as catalyst for the reduction of NO_x by NH₃ to form N₂ and H₂O as expressed below.



The treated flue gas exits the reactor and flows through the air heater, particulate removal, and FGD equipment before leaving the stack.

Once the CuO is converted to CuSO₄, the catalyst remains in this form for NO_x removal and, thus, SO_x in the flue gas passes through the reactor without being removed.

The reactor operating conditions are similar to those mentioned for the UOP simultaneous NO_x-SO_x removal process and are as follows:

Maximum particulate loading	Full loading (>10 gr/sft ³)
Pressure drop across the reactor	5-6 in. H ₂ O
NH ₃ :NO _x mol ratio	(1.0-1.2):1
Average space velocity	4,000-8,000 hr ⁻¹
Temperature	400°C (750°F)

NO_x removal efficiency of at least 90% is expected with 4-m-long beds and removal efficiencies of 95-97% and 99% have been achieved during prototype-scale testing on 6-m- and 7-m-long beds respectively.

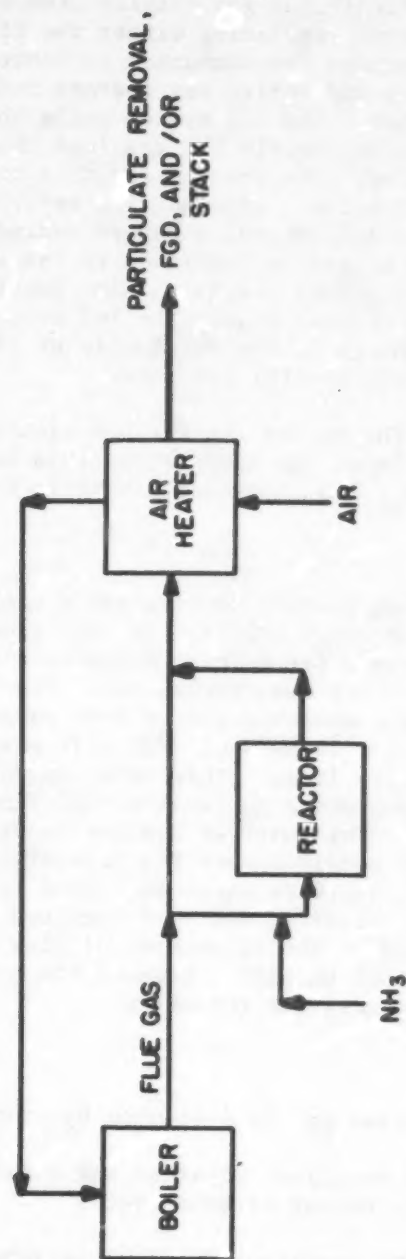


Figure 111. Flow Diagram of UOP Process.

There are several characteristics of this UOP NO_x-only removal process which are the same as for the UOP simultaneous NO_x-SO_x removal process. With this NO_x treatment system connected to the boiler system between the economizer and air heater, the most practical flue gas reaction temperature control method, though not the only way, involves regulating either the flow of flue gas or boiler feed water through or around the exchanger to control the heat transfer rate. Also, the FGT system and boiler may operate independently of each other with an open bypass system. The FGT system pulls the flue gas from the flue gas duct into its fan and expels the gas into the header to which the reactor inlets are connected. The treated gas then returns to the flue gas duct downstream of the FGT inlet. With no flow restriction in the flue gas duct between the FGT inlet and return, a bypass around the FGT unit is created. A continuous stream of gas is furnished to the reactors by the FGT fan regardless of the flue gas generation rate. Any excess flue gas from the boiler above the FGT fan rate may bypass the FGT system while gas may be recycled from the FGT discharge to the FGT fan inlet if the flue gas produced in the boiler is less than the FGT fan rate.

All the reactions occurring in the reactor are exothermic and by having the FGT system located upstream of the air heater, this heat of reaction is recoverable from the flue gas. Fan compression heat is recoverable too.

Status of Development

Shell began laboratory bench-scale testing and a catalyst search and desulfurization process in the early 1960's. In 1967 a unit of 0.2-0.3-MW capacity was built near Rotterdam (at Pernis) which used a parallel-passage reactor and unit cell acceptor for desulfurization. The fuel source was high-S fuel oil. This unit was operated over a 4-yr period for more than 20,000 cycles. In August 1973 a 40-MW equiv-FGD unit was placed on stream at Showa Yokkaichi Sekiyu (SYS), Japan. This unit was designed for flue gas containing 2500 ppm SO₂ and processes gas from an oil-fired boiler. About 90% SO₂ removal was obtained. This unit at SYS has functioned with simultaneous NO_x-SO_x removal since mid-1975 when NH₃ injection equipment was permanently installed. Also, a 0.6-MW equiv-FGD pilot plant of Tampa Electric Company (TECO) in Tampa, Florida, has been operated for 3 yr on coal-fired flue gas from 3.5% S coal. The slipstream of flue gas was taken either upstream or downstream of the ESP. Some of the demonstrated results from the above operations includes the following.

Pernis

- The preferred regeneration gas is a diluted H₂-containing gas
- The acceptor possessed excellent physical and chemical stability and will have a life in excess of 8000 cycles
- Corrosion rates with FGD conditions were established for a number of metals
- Pressure drop across the reactor remained low and constant

SYS

- Unit cells were handled and loaded into reactors with no difficulty
- Actual performance closely matched results from computer program simulating commercial performance indicating the usefulness of computer programs for reactor design and design optimization
- Engineering scaleup consists mainly of paralleling standardized unit cells
- The unit is operated by an automatic sequence controller requiring practically no operator attention after startup periods
- Special valves functioned properly to isolate reactors during regeneration
- Open bypass performs as intended to make FGT and boiler operations independent of each other

TECO (In addition to some items already stated for SYS)

- Acceptor is chemically and physically stable after 13,000 cycles (equivalent to a 3-yr life) with 90% SO₂ removal in 4-m bed and pressure drop of 5-6 in. H₂O
- Process performed well with particulate loading equal to 10 gr/sft³ (about 23 g/Nm³); in situ cleaning of reactor internals was found to be needed and a method was developed

This NO_x-only removal process has been tested on pilot plants and the 40-MW equiv prototype-scale SYS unit with the acceptor material completely in the form of CuSO₄.

Background of Process Developer

Shell International Petroleum Company developed this process and has been involved in this program since the early 1960's. The UOP Process Division holds the worldwide licensing rights to the Shell FGD process (with the exception of the Far East). The Shell FGD system is commercially available for oil-fired boilers. The simultaneous NO_x and SO₂ removal has been used at SYS unit since 1975 on oil-fired boiler while the TECO pilot plant has operated on a coal-fired flue gas for 3 yr. This process is readily accessible to the U.S. market.

Published Economic Data

The reported capital investment for an NO_x-only removal system treating flue gas from a 500-MW plant is \$31/kW (92). For the same facility, the reported revenue requirement is 1.4 mills/kWh (92). A midwestern U.S. location and mid-1977 erection charges provide the basis for the above economic

values. The parameters characterizing this NO_x removal system are as follows:

Flue gas to reactors, Nm ³ /hr	1,582,000
Temperature of flue gas, °C	400
SO ₂ content, ppm	2,580
NO _x content, ppm	634
NO _x removal, %	90
Number of reactors	4
Bed length, m	4
Reactor diameter, m	8.70
Catalyst quantity, kg/reactor	51,480
Pressure drop across system, cm H ₂ O	23

Raw Material, Energy, and Operation Requirements

The raw material and energy requirements for the above 500-MW case are as follows:

<u>Material</u>	<u>Quantity</u>
NH ₃	21 short tons/day
Electricity	3,242 kW
Steam	13.2 short tons/day

The total electrical usage equals about 0.6% of the equivalent power output of the 500-MW plant. Also, a heat credit constituting 26.5 MBtu/hr is reported for fan compression and reaction heat recoverable at the air heater.

The labor and supervisory requirements for the same 500-MW example are reported as 1750 hr/yr at an average cost of \$8/hr. This represents an annual cost of \$14,000. The maintenance needs are reported to cost \$194,000 annually. UOP reported that no additional manpower was needed for the 40-MW equiv-unit at SYS and that the operator control needed was practically nil after startup and the initial operating period.

Technical Considerations

The UOP Shell CuO process for NO_x-only removal is simple requiring only a reactor, NH₃ storage, and injection equipment. The NO_x-only removal system represents significant reduction in complexity, number of operation steps, and capital and operating costs in comparison to the UOP simultaneous NO_x-SO₂ removal system.

The NO_x removal efficiency is reported to be independent of inlet gas NO_x concentration. The NO_x reaction is first order and the NO_x reaction rate is directly proportional to the NO_x concentration. The NO_x removal rate will increase as bed length increases.

The reactor size may be about average for dry SCR systems since the reaction temperature is similar and assuming the space velocity ranges from 4000 hr⁻¹ to 8000 hr⁻¹. The number of reactors reportedly needed for the 500-MW example is four.

The UOP NO_x-only removal system is suitable for retrofit on a plant with or without an FGD system. Of course, reheat will be needed for the system located after the air heater. Also, more reheat is required if the NO_x removal system is placed after rather than before a low-temperature FGD unit.

There are no byproducts made with this process.

With the open bypass system the turndown ratio is unlimited, capable of operating from full boiler load to complete recycle.

The materials of construction are considered proprietary information; however, UOP states that no unusual materials are used. UOP has derived corrosion rates for various metals under FGD reactor conditions. Service life of at least 15 yr for the reactor internals has been estimated with the proper construction materials.

Environmental Considerations

NO_x removal data from tests at pilot plants and the prototype-scale (40 MW equiv) unit at SYS are shown in Figure 112. The acceptor used was completely in the sulfated form. The results are plotted as a function of bed length since NO_x conversion fluctuated with time on stream, reactor internals design, and operating conditions. NO_x removal efficiencies of 95-97% for 6-m-length beds and 99% for 7-m-length beds have been obtained during tests.

No waste disposal is needed for this system. The NH₃ exiting with the treated gas reportedly averages 1 ppm.

The parallel-passage reactor has been shown capable of operating at normal conditions with full particulate loading (>10 gr/sft³). Initial testing with full flyash loading to the reactor at the Pernis unit showed no deterioration in performance. However, at SYS the high V- and Na-containing flyash gradually fouled the reactor internals forcing runs to be limited to operating periods of 1-2 mo. The higher particulate loading with coal-fired flue gas at TECO of 10 gr/sft³ or greater, caused a decline in performance after only days of operation. As a result of this problem, a procedure was developed and implemented at this pilot plant which provided in situ cleaning of reactor internals during normal operation. This technique allowed stable performance with high particulate loadings; pressure drop across the reactor and desulfurization were not affected. Cleaning of reactor internals will be implemented at SYS also.

Testing at TECO also demonstrated that Cl₂ and Cl⁻ in flue gas had no adverse effect upon the acceptor performance. The loss of Cu was negligible.

Critical Data Gaps and Poorly Understood Phenomena

Although there are no major poorly understood phenomena, the use of an Al₂O₃ base for the CuSO₄ catalyst is questionable since there is a trend of

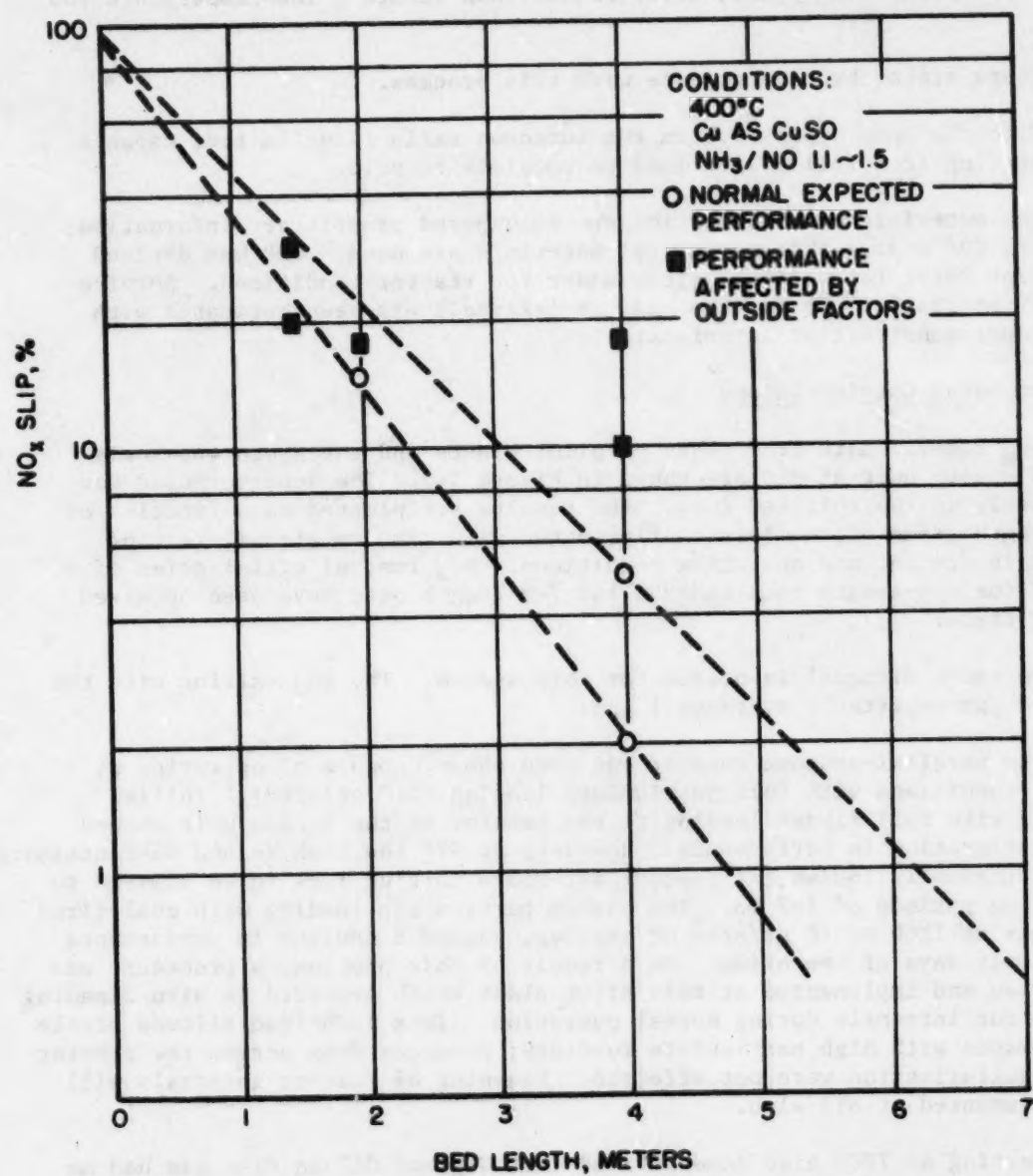


Figure 112. Unconverted NO_x as a Function of Catalyst Bed Length for UOP Process (92).

competing processes to be changing to alternate, supposedly more stable supports. It is recognized that UOP refers to their catalyst as being on a "special" Al_2O_3 support.

Advantages and Disadvantages

The advantages and disadvantages of the UOP-Shell CuO NO_x -only removal process are as follows:

Advantages

1. Achieves >90% NO_x removal efficiency
2. Has been applied to flue gas from commercial oil-fired boilers
3. Is a slight modification of a commercially available FGD system
4. Operates with full particulate loading ($>7\text{gr/sft}^3$)
5. Claims <10 ppm by vol NH_3 in treated flue gas
6. Claims full turndown capability

Disadvantages

1. Has not been tested on coal-fired flue gas

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Although much development work has been performed for flue gas denitrification, most processes have been developed only through bench-scale or pilot-plant operation using flue gas from gas- or oil-fired sources. The most tested and advanced type of FGT process is now SCR. Several commercial, oil-fired SCR denitrification facilities have been operated; about half of the NO_x removal processes included in this report are the SCR type. The majority of the SCR processes are reportedly capable of excellent NO_x removal (>90%). Looking at other dry methods of NO_x removal, the selective noncatalytic example (Exxon Thermal) has been tested on a commercial oil-fired boiler but the NO_x removal efficiency achieved may only be 60-70%. The dry, adsorption process (Foster Wheeler) has been tested on a coal-fired flue gas at a prototype unit. However, NO_x removal efficiency was only 25-30%. The Ebara-JAERI radiation process has reached the pilot-plant status and may remove about 90% of the NO_x . The major drawbacks with the dry flue gas denitrification schemes which will require attention in future testing on coal-fired sources are the sensitivity to particulates in all dry processes and the formation of NH_4HSO_4 for NH_3 -reductant processes.

Though not as well developed as SCR methods, the oxidation-absorption-reduction method is the most advanced wet NO_x removal method. Two of the oxidation-absorption-reduction processes have been tested on prototype units, with the remainder having been tested on bench-scale or pilot-plant units. Reportedly, these processes obtain moderate NO_x removal (80-90% efficiency). The absorption-reduction processes have only reached bench-scale or pilot-plant status with 60-85% NO_x removal efficiency. Of these processes, only PENSYS has been tested on coal-fired flue gas. Of the oxidation-absorption processes which have been tested, one has operated on a prototype unit and the other has operated on a pilot plant with coal-fired flue gas with no published results to date. Of the absorption-oxidation processes, only pilot-plant studies or smaller are presently active. The major adverse factors to be considered with wet processes in future testing include waste stream treatment, expensive oxidants, and the complicated series of processing steps which are usually required.

The reported economics vary greatly for these NO_x removal processes, even when the processes are within the same classification. The economics are given as reported from the process developer and represent various bases which impairs any meaningful comparison. Revisions in the economics may be expected as further testing is accomplished on larger facilities.

It is concluded that several adverse process characteristics should be considered in future development regarding both dry and wet NO_x removal processes. In addition, further testing must be done on pilot-plant and prototype units with coal-fired flue gas before any FGT processes are considered feasible by the utility industry for commercial, coal-fired power plant application.

One purpose of this first phase of the NO_x removal process study has been to perform a state-of-the-art review of all the flue gas denitrification systems currently undergoing development. The primary evaluation criteria were the technical and commercial feasibilities of each of these denitrification processes. Once this initial technical survey of all of the processes had been completed, the most viable processes were selected for preliminary economic analysis in the second phase of the study. These selected processes, which are listed in Table 30, have been chosen based on three criteria.

- Technical considerations
- Development status
- Representative sample

TABLE 30. PROCESSES SELECTED FOR FURTHER STUDY IN PHASE II

Process	Type of process (classification)
UOP Shell Copper Oxide	Dry simultaneous SO ₂ -NO _x (Selective catalytic reduction)
UOP Shell Copper Oxide	Dry NO _x only (Selective catalytic reduction)
Hitachi Zosen	Dry NO _x only (Selective catalytic reduction)
Kurabo Knorca	Dry NO _x only (Selective catalytic reduction)
Moretana Calcium	Wet simultaneous SO ₂ -NO _x (Oxidation-absorption-reduction)
Ishikawajima-Harima Heavy Industries	Wet simultaneous SO ₂ -NO _x (Oxidation-absorption-reduction)
Asahi Chemical	Wet simultaneous SO ₂ -NO _x (Absorption-reduction)
MON Alkali Permanganate	Wet NO _x only (Absorption-oxidation)

Each of these selection criteria is probably obvious except for the third, representative sample. There are five different types of dry processes and four types of wet processes in various stages of development and an attempt was made to select one process from each type. Thus, in addition to selecting the best processes from the standpoint of both technical feasibility and development status, an attempt was made to select only the best process, based on these two criteria, from each type of flue gas denitrification process. A preliminary economic analysis of differing types of processes in the second phase would allow a fair comparison between the various technologies available for flue gas denitrification. This broad coverage would also prevent possible later questions on why certain types of flue gas denitrification processes were dropped from consideration simply because they had only been tested in a bench-scale unit.

TECHNICAL CONSIDERATIONS

The primary consideration involved in selecting processes for further study was whether the process was technologically feasible, i.e., whether the basic reactions and operations involved in the process were either well-known or had been demonstrated in actual operation. With the exception of three processes, all of the denitrification systems included in this study have been tested on oil-fired flue gas. Thus most of these processes have demonstrated their capability in treating clean flue gas.

Since coal is the primary utility boiler fuel in the U.S. and is expected to be used almost exclusively in all new fossil-fueled utility boilers, a second technical consideration is the ability of the process to handle the increased particulates, SO_x , NO_x , and Cl^- levels associated with coal combustion. Although essentially all of the development work for these denitrification processes have been done on oil-fired flue gas, most of these processes are expected, with minor modifications, to be able to handle the flue gas from coal-fired boilers. With the addition of either an efficient hot ESP (primarily for the dry processes) or a closed-loop prescrubbing section (primarily for the wet processes), the particulate problem is expected to be controlled. In addition, most of the dry processes have developed catalysts or designed reactors which minimize the effects of dust, i.e., the catalysts in packed-bed reactors are either honeycomb, ring, or pipe shaped or if the catalyst particles are present in pellet form they are packed in either a moving-bed reactor or a reactor with a specially designed internal structure.

For the dry NO_x -only processes increasing the NO_x concentration in converting from oil-firing to coal-firing will increase the NH_3 consumption rate and, hence, substantially affect the economics of the process. However, from a technical point of view the increased NO_x concentration should not cause any problems. The increased levels of the SO_x are also not expected to have a significant impact on the dry NO_x -only processes. The Cl^- , however, depending on its actual chemical makeup, may present problems by reacting with the catalyst particles.

For the wet simultaneous SO_2 - NO_x processes with a prescrubber, the increased particulates, SO_x , NO_x , and Cl^- in the flue gas are expected to only have a minimal impact from a technical standpoint.

Although the projected economics of each of these processes would be a valuable addition to the selection criteria, the economic data included for most of these processes are estimates made by the process developer and as such are based on widely ranging premises. Any attempt to convert these estimates to a single standard set of premises without investigating the estimate details to determine the items covered would only add additional uncertainties, such that all the resulting calculated values would be essentially equivalent within the errors of uncertainty. For this reason, the processes were not selected based on their projected economics.

DEVELOPMENT STATUS

The second major selection criteria was the development status of the process. The development status was chosen since it reflects a degree of achieving full-scale commercial operation and also indirectly the confidence level which the process developers have in the technical and economic feasibility of their system. Ideally, the development of the selected process would have reached the commercial stage (>50 MW) and be treating flue gas from a coal-fired boiler. However, since only one or two of the processes have been extensively tested on coal-fired flue gas, this selection criteria was reduced to simply the size of the unit in which the process was currently being tested. For the purposes of this study, the following size ranges have been defined for each stage of development.

<u>Stage of development</u>	<u>Size of unit</u>
Commercial	MW ≥ 50
Prototype	$5 \leq$ MW < 50
Pilot plant	$0.5 \leq$ MW < 5
Laboratory	MW < 0.5

Each of the flue gas denitrification processes included in this study have been arranged in order in Table 31 according to their current status of development. As is readily apparent from this table, the various processes are equally divided between the commercial, prototype, pilot plant, and bench-scale units. However on closer examination, those processes currently at the commercial or prototype stage of development are either the dry SCR or the wet, oxidation-absorption-reduction type. Thus if the process selection was based entirely on the current status of development, only two types of flue gas denitrification processes would have been represented. At the completion of the second phase of the NO_x process study, the preliminary economic analysis, a comparison of only these two types of NO_x removal processes would be available. A comparison between wet NO_x -only and dry NO_x -only processes would not be available and a comparison between the economics of wet oxidation-absorption-reduction processes using a gas-phase oxidant and the wet, absorption-reduction not using a gas-phase oxidant would be impossible since the absorption-reduction processes in general have not

TABLE 31. STATUS OF DEVELOPMENT
OF THE FLUE GAS DENITRIFICATION PROCESSES

Process	Size, MW equivalent
<u>Commercial scale</u>	
Hitachi Zosen	275
Hitachi, Ltd.	170
Sumitomo Chemical	100
Mitsui Engineering and Shipbuilding (Dry)	67 ^a
Exxon Thermal Denox	53
<u>Prototype-scale</u>	
Moretana Sodium	40
UOP (NO _x -SO ₂)	40
UOP (NO _x -only)	40
Tokyo Electric-Mitsubishi Heavy Industries	33
Mitsui Toatsu	30
JGC Paradox	23
Foster Wheeler-Bergbau Forschung	20
Kobe Steel (Wet)	17 ^b
Kurabo Knorca	10
Moretana Calcium	8.3
<u>Pilot-plant scale</u>	
Mitsubishi Kakoki Kaisha	4.7
Takeda	3.3
Sumitomo Heavy Industries (NO _x -SO ₂)	3.3
Ishikawajima-Harima Heavy Industries	1.6
Kawasaki Heavy Industries	1.6
Kureha (Wet)	1.6
Kureha (Dry)	1.6
Pittsburgh Environmental and Energy Systems	1.6 ^a
Eneron	1.5
Unitika (NO _x -SO ₂)	1.5
MON Alkali Permanganate	1.3
Mitsubishi Heavy Industries (Dry)	1.3
Ebara-Jaeri	1.0
Mitsubishi Heavy Industries (Wet)	0.6
<u>Bench-scale</u>	
Sumitomo Heavy Industries (NO _x -only)	0.5
Chiyoda Thoroughbred 102	0.3
Kobe Steel (Dry)	0.3
Chisso Engineering	0.10
Unitika (NO _x -only)	0.07
Mitsui Engineering and Shipbuilding (Wet)	0.05
Asahi Chemical	0.02
Exxon (SCR)	0.003
<u>Not tested on flue gas</u>	
Nissan Engineering	-
Ralph M. Parsons	-
Ube (Dry and Wet)	-
Mitsubishi Petrochemical	Uncertain

a. Under construction

b. Terminated (new process under development).

reached the pilot-plant stage. Thus by only considering the status of development, many important and perhaps fundamental comparisons would be eliminated. Therefore, the third selection criterion given in the following section was incorporated into the evaluation section.

REPRESENTATIVE SAMPLE

During the selection processes, the above-mentioned criteria, i.e., the technical considerations and the status of development, were modified in order to obtain a representative sample of all the types of flue gas denitri-fication processes currently undergoing development. In other words, attempts were made to select the best process from each type of treatment scheme if that process was deemed technologically feasible. For example, although the Asahi Chemical process has only been tested in a laboratory-scale unit, it represents substantially different technology than the other selected processes. In addition, it is fairly representative of an entire class of NO_x removal processes that, based on the other selection criteria, would not be acceptable for further study in Phase II. Although an example of each of the various technologies could not be selected, those categories which are not represented among the selected processes were categories which only had one or two example processes. Thus those categories did not represent a sizable portion of the current NO_x FGT technology.

The selection of two wet, oxidation-absorption-reduction processes, as shown in Table 30, appears to be consistent with the specific purposes of having a representative sample. However, these two oxidation-absorption-reduction processes, the Moretana Calcium and the Ishikawajima-Harima, have a major difference in that in the former ClO_2 is used as the gas-phase oxidant where as Ishikawajima-Harima has chosen O_3 as the gas-phase oxidant. These two oxidants, although serving the same purpose, offer substantially different complications in both their generation equipment and the resulting processing scheme and, therefore, different costs and technologies. Thus, the selection of these two processes is consistent with the avowed purpose of obtaining a representative sample.

Similar differences are noted in the dry NO_x removal processes. The UOP Shell CuO system represents a unique process for two reasons. This process can operate not only as a dry, NO_x -only removal system, but also as a dry simultaneous SO_2 - NO_x system which allows a comparison of both types of dry process with a somewhat simplified calculation. The second reason for selecting the UOP process is that it has a parallel passage reactor design which minimizes the adverse effects of the heavy particulate loading in the coal-fired flue gas. This reactor system has also been tested on coal-fired flue gas, although only in the FGD mode.

Both the Hitachi-Zosen and the Kurabo processes are based on the SCR of NO_x using NH_3 , but they have one fundamental, and therefore important, difference. The Hitachi-Zosen process uses a typical fixed-bed reactor containing a honeycomb-shaped catalyst to prevent excessive plugging by the dust in the flue gas, whereas the Kurabo process is based on a continuous moving-bed reactor containing spherical-shaped catalyst particles. Thus, by

including both the Hitachi-Zosen and the Kurabo processes in the preliminary economic analysis phase, a general comparison of the moving-bed reactor with a fixed-bed reactor for NO_x removal will be possible.

If sufficient funding to select three additional processes were available, the following dry processes could be included for further study: the Ralph M. Parsons, the Exxon Thermal, and the Takeda. The Ralph M. Parsons process is a nonselective catalytic reduction process and, hence, would result in a direct comparison of nonselective with selective catalytic reduction. The evaluation of the Exxon Thermal process would be a good example for comparison in that the NH_3 is injected directly into the boiler to selectively reduce the NO_x and thus eliminate the need for an add-on catalytic denitrification system. The Takeda process, since it is based on both SCR of NO_x and activated C adsorption of SO_2 , would provide a comparison of base-metal catalysts with the activated-C-type reduction process for SCR as well as for comparison of differing dry simultaneous SO_2 - NO_x processes.

It should be pointed out that in some cases there are several other processes equivalent to those chosen for further study in Phase II. Their elimination should not be construed as adverse comments on these processes, but only as representing similar technologies that do not possess significant differences from those processes selected. For example, the Ishikawajima-Harima process was chosen as the representative for the O_3 -based oxidation-absorption-reduction processes but several others would be equally well representative of this group, including Mitsubishi Heavy Industries process and possibly the Chiyoda Thoroughbred 102 process. The Mitsui Engineering and Shipbuilding dry process is similar to the Hitachi-Zosen process and the Kobe Steel process is similar to the Kurabo process, but, because of the scope of the second phase, only one of each type could be selected. Within the errors of calculation, the results obtained in the preliminary economic analysis for the selected processes would be applicable to these processes which were not selected.

RECOMMENDATIONS

From the preceding conclusions a more detailed analysis, including process design and preliminary economics, for the eight selected NO_x removal processes is recommended to be included in the second phase of this study. Premises will be chosen such that a uniform comparison of each selected NO_x removal system will be obtained for a single case. The general premises for this process design and preliminary economic study will be established on a new, 500-MW coal-fired power plant burning coal with 3.5% S (dry basis). The NO_x and SO_x emissions in the untreated flue gas will be about 600 ppm and 2400 ppm by vol respectively.

During Phase II the process design for each selected method will include the following: process flow diagram material and energy balances, fuel stream requirements and waste treatment needs. The preliminary economics will include both capital investments and revenue requirements. The capital investment based on mid-1979 dollars will encompass costs for major equipment site preparation and installation labor and material for electrical, ductwork,

pipng, etc. The revenue requirements will be based on mid-1980 dollars. This section will contain annual revenue requirements and also projections for the availability and cost of process reagents as a function of time.

With these recommendations, Phase II studies will provide a direct comparison of the various flue gas denitrification technologies. The results should establish which of the following alternatives are more economically promising.

- | | | |
|-----------------------------|----|--|
| 1. NO absorption | vs | gas-phase oxidation |
| 2. Wet simultaneous process | vs | dry simultaneous process |
| 3. Wet simultaneous process | vs | wet FGD + dry, NO _x -only process |
| 4. Wet NO _x only | vs | dry NO _x only |
| 5. Dry simultaneous | vs | wet FGD + dry, NO _x -only process |

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APPENDIX A

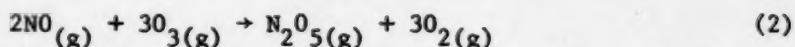
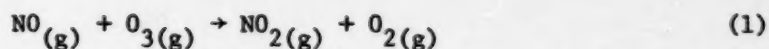
GAS-PHASE OXIDATION OF NO

APPENDIX A

OXIDATION OF NO

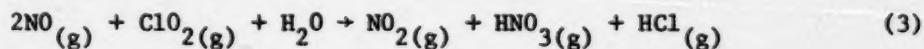
The easiest and cheapest method of converting insoluble NO to NO₂ would be to react the NO with the excess O₂ already present in the flue gas. Although the oxidation of NO by free O₂ in the flue gas is theoretically possible, in actual boiler operations there is insufficient reaction time during the passage from the boiler to the stack. For the 95-100% conversion of the NO in the flue gas by free O₂ as required in the oxidation processes, the residence time necessary in the system would be on the order of 1 hr. Thus, for practical operations a method to promote the oxidation rate is required.

The primary method of increasing the oxidation rate of NO currently undergoing development is through the use of gas-phase oxidant. These gas-phase oxidants are capable of rapidly and selectively oxidizing the NO with reaction times on the order of half a second. The two gas-phase oxidants currently being considered are O₃ and ClO₂. The use of O₃ results in the following reactions:



With good distribution of the O₃ into the flue gas duct, reaction (2) can be minimized and better O₃ utilization can be achieved. O₃ is favored by many process developers since its use generates no undesirable byproducts in the flue gas and the equipment required for the generation of O₃ is relatively simple and easy to control. The primary disadvantage of using O₃ as the gas-phase oxidant is the expense involved in generating the O₃.

ClO₂ also rapidly oxidizes NO at a reaction rate similar to that of O₃. The use of ClO₂ results in the following gas-phase reaction:



The use of ClO₂ is favored by some since, as compared to O₃, it is cheaper to produce and also because 1 mol of ClO₂ oxidizes 2 mols of NO. In addition, ClO₂ converts 1 mol of NO into HNO₃ which is much more soluble than NO₂. The disadvantages associated with the use of ClO₂ include the high cost of ClO₂, the formation of undesirable reaction products such as HCl and HNO₃ in flue gas, and the extensive chemical processing system involved in generating ClO₂. This generation of ClO₂ by chemical reaction also results in the slow response to changing levels of NO_x in the flue gas.

Brief introductions to the technical and economic considerations for both O_3 and ClO_2 generating systems follow.

O_3 GENERATION

Since most of the oxidation-absorption-reduction processes under current development favor O_3 as the gas-phase oxidant to convert relatively insoluble NO to NO_2 , the following discussion is included to briefly describe O_3 generation technology and costs. Other sources of information on O_3 are available for a more detailed explanation of the technology. (J. W. Harrison, Technology and Economics of Flue Gas NO_x Oxidation by Ozone Research Triangle Institute, Research Triangle Park, North Carolina 27709, November 1976.)

O_3 can be generated by any of five relatively exotic methods including electrolysis of H_2O , photochemical reaction, radiochemical reaction, thermal reaction, and corona discharge in either air or O_2 . The least expensive and the most common method for generating O_3 on the scale required for commercial-sized FGT systems would be corona discharge in air or O_2 . In this method either air or O_2 is fed to a bank of O_3 generators (see Figure A-1 for a diagram of a typical O_3 generator) where, under a pressure of 1.2-2.0 atmosphere, an electrical discharge is passed through the feed gas. If the feed gas is air, the resulting exit gas stream will contain approximately 1% (by wt) O_3 and, if O_2 is used, the exit stream will contain 1.5-2.0% (by wt) O_3 . The yield of O_3 per unit of energy also depends on the feed gas: for air feed approximately 0.05-0.06 kg (0.11-0.13 lb) of O_3 are produced per kWh, while for O_2 feed about 0.11-0.13 kg (0.24-0.29 lb) of O_3 are produced per kWh of electricity. Although at first glance it would appear that generating O_3 from O_2 would be more economical; if the cost of the O_2 plant is included, the air-feed system is more economical. This is readily apparent from the costs given in Table A-1. Thus for a coal-fired boiler generating flue gas containing 600 ppm NO_x , the air-feed O_3 generator system itself adds \$53/kW to the capital cost of the plant and 4.7 mills/kWh to the annual revenue requirements for the SO_2 - NO_x removal system. (Cost basis: assumed U.S. and 1976 dollars). The use of O_2 as the feed stream would approximately triple both the capital cost and annual revenue requirements for the O_3 generating system.

In addition Table A-1 also includes a comparison of the O_3 generating costs for treating flue gas from a coal-fired boiler containing 600 ppm NO_x and for treating flue gas from an oil-fired boiler containing 200 ppm NO_x . In Japan where most of these processes were developed, most of the boilers are fired with oil and hence capital costs and annual revenue requirements are only one-third those required for treating coal-fired flue gas.

The O_3 generating system using air feed consists of two stages as shown in Figure A-2: a preparation stage including filters, coolers, and driers to remove the particulates and H_2O from the air and the actual O_3 generation section. The air must be dried to a dew point of at least $-60^\circ C$ ($-77^\circ F$) since the presence of H_2O in the air stream can result in both sparking and also the decomposition of the O_3 . If H_2O is present in the air stream it can also react with the small amount of N_2O_5 produced in the O_3 generator to form HNO_3 . If the more expensive O_2 -fed system is used, however, these problems are eliminated since the O_2 plant produced a clean, dry O_2 stream.

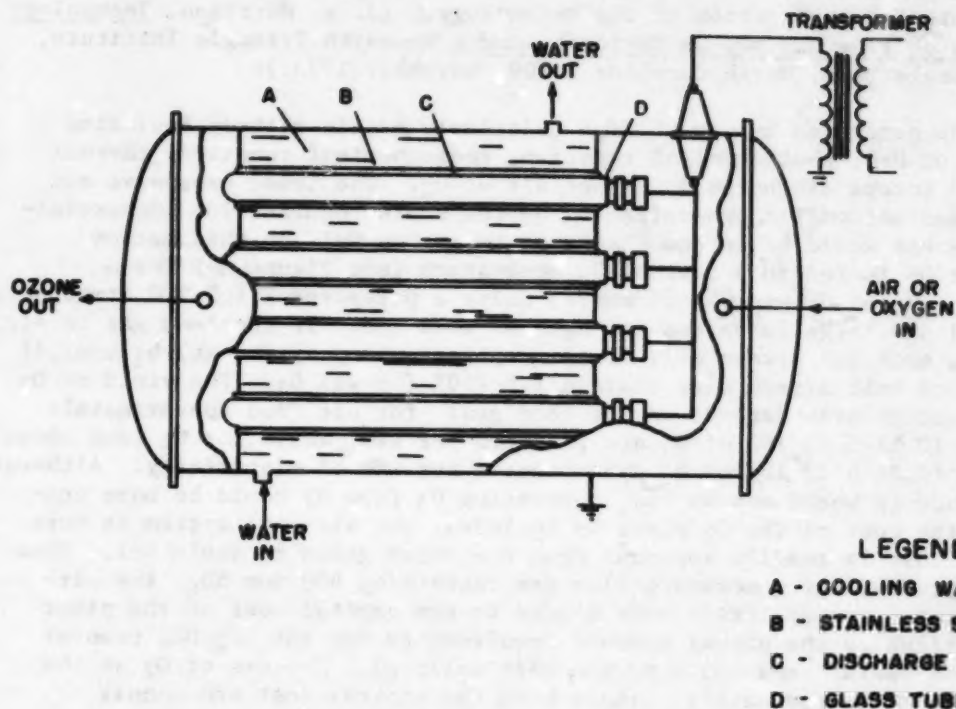
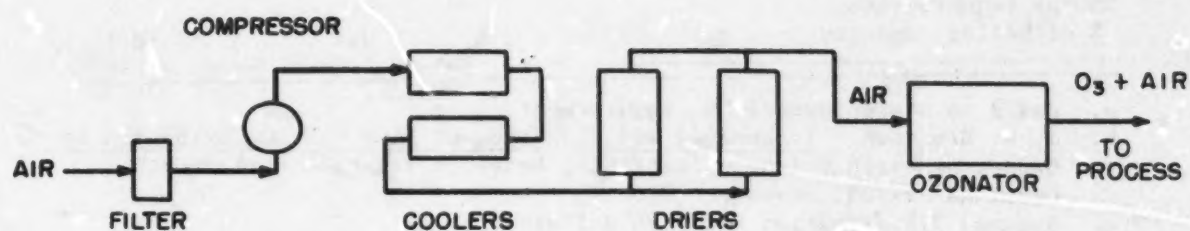
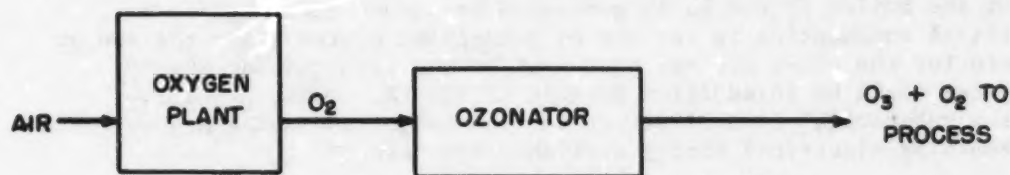


Figure A-1. Welsbach Ozonator (49).



OZONE FROM AIR



OZONE FROM OXYGEN

Figure A-2. Ozone Generation Systems (49).

TABLE A-1. SUMMARY OF CAPITAL INVESTMENT, REVENUE REQUIREMENTS, AND
ENERGY REQUIREMENTS FOR THE OXIDATION OF FLUE GAS NO BY
O₃^a IN 500-MW OIL-FIRED AND COAL-FIRED PLANTS^b

Item	Oil fired (200 ppm NO)		Coal fired (600 ppm NO)	
	Air feed	O ₂ feed	Air feed	O ₂ feed
Capital investment, \$/kW ^c	17.60	56.20	52.60	152.40
Revenue requirements, mills/kWh ^c	2.0	3.8	4.7	9.1
Energy requirements, % of boiler capacity	3.1	3.6	9.4	10.7

a. Based on stoichiometric O₃ requirement.

b. J. W. Harrison. Technology and Economics of Flue Gas NO_x Oxidation by Ozone, Research Triangle Institute, Research Triangle Park, North Carolina 27709, November 1976.

c. Assumed U.S. location and 1976 dollars.

For a 500-MW coal-fired power plant generating flue gas containing 600 ppm NO_x, the requirement for 90% NO_x removal will result in an estimated electrical consumption of 47,500 kW or approximately 9.4% of the generating capacity of the boiler if the O₃ is generated by corona discharge in air. This electrical consumption is for the O₃ generating system only; the energy requirements for the other process equipment in the simultaneous SO₂-NO_x removal system would be in addition to this 47,500 kW. This, of course, represents a substantial loss of output for the boiler and hence higher costs for the remaining electrical energy available for sale.

The O₃ generating system, in addition to its high electrical consumption, also requires significant quantities of cooling H₂O and process air. Since about 90% of the electrical energy consumed to produce the O₃ is rejected as waste heat, the cooling water requirement for the 500-MW boiler system is substantial (approx 550 gpm). Failure to adequately remove this waste heat increases the rate of O₃ decomposition and hence would increase the already high energy cost for each unit of O₃. The air feed rate to the O₃ generators for this 500-MW coal-fired boiler would be approximately 100,000 sft³/min. Not only will this high air feed rate require large and expensive pieces of process-handling equipment but the injection of this much air into the flue gas ducts represents a 6.5% increase in the amount of gas to be scrubbed and of course reheated. The adverse ramifications of this increase in flow rate on the process economics have not been studied as yet.

One other major technical consideration concerning the O₃ generation section is the relatively small capacities of the O₃ generators currently available. The largest commercial O₃ generators available at the present time have a rated capacity of only 560 kg (1232 lb) of O₃/day. Since a

500-MW coal-fired boiler based on the premises of this study (600 ppm NO_x in the flue gas and 90% NO_x removal) would require approximately 49,000 kg (107,700 lb) of O_3 /day, each 500-MW boiler would require a battery of at least 88 individual O_3 units rated at 560 kg of O_3 /day. Assuming a 10% excess capacity factor, a minimum of about 100 O_3 generators would be required in the battery for a 500-MW coal-fired boiler.

ClO_2 GENERATION

Although most of the oxidation-absorption-reduction processes use O_3 as the gas-phase oxidant, the processes offered by Sumitomo Metals (Moretana Calcium and Sodium processes) opt to use ClO_2 to oxidize NO to NO_2 . Even though the use of ClO_2 results in the introduction of high levels of Cl^- in the circulating solution and increased amounts of effluent wastewater, it is much cheaper to use since each mol of ClO_2 oxidizes twice as many mols of NO as each mol of O_3 and also because the cost/mol of oxidant, although still expensive, is less for ClO_2 .

Since ClO_2 is a commonly used industrial chemical, particularly in the paper industry, numerous methods of producing it have been developed over the years. However, most of these processes developed by the paper industry result in the production of Na_2SO_4 which can be reused in the pulping process but which cannot be used in this SO_2 - NO_x removal process. The Kesting process generates byproduct NaCl which can be used to regenerate NaClO_3 , but unfortunately this process also generates relatively large amounts of undesirable Cl_2 gas. Thus, Sumitomo Metals and DAISO Engineering developed a modified version of the Kesting (HCl) process for the simultaneous SO_2 - NO_x removal system in which an additive is used to minimize the formation of free Cl_2 in the outlet gas. NaCl , HCl , and the proprietary additive are reacted to generate a weak (3% by vol) ClO_2 gas stream and a recycle Na salt solution. This salt solution is recycled and undergoes electrolysis to regenerate the required NaClO_3 to complete the cycle. The only raw materials required appear to be NaOH , HCl , and the additive.

Under the premises of this study (90% NO_x removal and 600 ppm NO_x) a 500-MW coal-fired power plant would consume approximately 46-51 tons/day of ClO_2 depending on the ratio of ClO_2 : NO_x used (46 tons/day corresponds to a ClO_2 : NO_x = 0.55 and 51 tons/day to ClO_2 : NO_x = 0.60). The ClO_2 required for an oil-fired boiler flue gas containing 200 ppm NO_x would be proportionately less, i.e., 15-17 tons/day depending on the ClO_2 : NO_x ratio. Although the capital investment and the annual revenue requirements for the Sumitomo-DAISO ClO_2 generating system have not been released, a similar capacity (50 tons/day) ClO_2 generating system using the Hooker R-2 method has been estimated (E. S. Atkinson, Hooker Chemicals & Plastics Corporation, Niagara Falls, N. Y., Private communication, May 1977) as \$2.0M for the capital investment (\$4/kW) and an estimated \$8.8M for the annual revenue requirements (2.51 mills/kWh). (Cost basis: assumed U.S. and 1976 dollars).

One of the main drawbacks associated with the use of ClO_2 as a gas-phase oxidant is the very slow response of the system to changes in the NO_x concentration of the inlet flue gas. Since the ClO_2 is generated by chemical

reaction and cannot be stored, an abrupt increase in the NO_x concentration in the inlet flue gas cannot be treated effectively for a period of time as the ClO_2 generator gradually increases production. Although the average NO_x removal efficiency can be high, whenever the inlet NO_x concentration increases sharply, the removal efficiency can drop and remain at lower levels during the time required for the ClO_2 generating system to increase production.

Although the amount of inert material injected with the ClO_2 results in a large gas stream (13,600 aft^3/min at 127°F), it is only one-tenth the size of the gas stream used for the O_3 injection system and represents an increase of <1% in the total amount of gas to be scrubbed and consequently reheated.

APPENDIX B

SOLUBILITY OF VARIOUS GASES IN H₂O

TABLE B-1. SOLUBILITY OF VARIOUS GASES IN H₂O^a

Gas	Solubility (in g/l)
N ₂	0.010
O ₂	0.044
NO	0.063
NO ₂	1.26
CO ₂	1.74
H ₂ S	3.98
SO ₂	117.0

- a. J. N. Driscoll, Flue Gas Monitoring Techniques and Manual Determination of Gaseous Pollutants
Ann Arbor Science Publishers, Ann Arbor,
Michigan, 1974, pp. 219-263.